THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

FEBRUARY 1932.

XVI. *The Hall Effect and other Physical Properties of the Copper-Cadmium Series of Alloys.*

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Introduction.

THE present investigation is a continuation of the experiments on the Hall effects and other physical properties of binary alloys, carried out at the Physics Department of the University College of Swansea.

In recent years much attention has been paid to theories of electrical conduction in metals, but little progress has been made in their application to alloys. In order to test such theories it is essential in the first place to carry out measurements of the various galvanomagnetic and electrical properties on the same specimen of a pure alloy. In addition, if the measurements are to be of real value the alloys must be in a definite reproduceable state, which can only be realized by annealing them at the correct temperatures. Adequate data for this purpose is usually obtained from a careful study of the equilibrium

* Communicated by the Authors.

† Stephens and Evans, Phil. Mag. (Jan. 1929); Stephens, Phil. Mag. (Sept. 1929).

diagram of the binary system under investigation. The experimental results obtained in investigations carried out on the various physical properties of alloys can then be examined in relation to the appropriate equilibrium diagram. With these objects in view the present investigation dealing with the Hall effect and other physical properties of the copper-cadmium series of alloys were undertaken.

The nature of the curves showing the variation of any physical property of an alloy with composition depends largely on the constituents of the alloy. In some cases the curve is continuous, but in others it shows at definite compositions singular points indicating the probable presence of intermetallic compounds at these compositions.

The results are rendered more valuable when the structures of the alloys have also been determined by X-rays, as the various physical properties can then be correlated with known changes in the arrangements and distances apart of the atoms in the alloy. Sahmen*, who examined the equilibrium diagram of the copper-cadmium system, gave two compounds corresponding to Cu_2Cd and Cu_2Cd_3, but Jenkins and Hanson † in a later investigation found evidence for four compounds corresponding to Cu_2Cd, Cu_4Cd_3, Cu_2Cd_3, and $CuCd_3$. Other investigations dealing with the physical properties considered in this paper are those of Bornemann and Wagenmann ‡ on the resistivities of the copper-cadmium alloys at high temperatures, and of Budgen ‖ on the densities of the alloys at the copper end of the series.

In the present research the Hall coefficients, the electrical resistivities, the temperature coefficients of resistance, the thermoelectric powers, the specific heats, and the densities of the copper-cadmium alloys of various compositions have been determined.

The experimental results obtained for the different physical properties will be compared with one another and considered in relation to the equilibrium diagram (fig. 1).

* R. Sahmen, *Zeitschr. Anorg. Chemie*, xlix. pp. 301-310 (May 31, 1906).

† Jenkins and Hanson, Journ. Inst. Metals, xxxi. pp. 257-270 (1924).

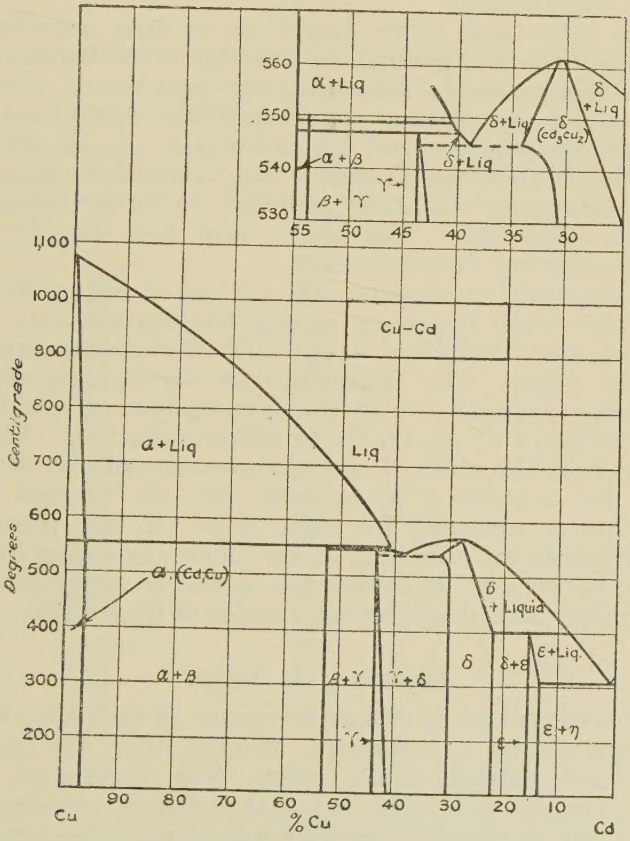
‡ 'Ferrum,' ii. p. 289 (1914).

‖ Budgen, 'Cadmium and its Alloys,' pp. 135-142.

Preparation and Annealing of the Alloys.

The copper-cadmium series of alloys used in this investigation was prepared in the Physical and Metallur-

Fig. 1.



gical Departments of the University College of Swansea. The copper used in their preparation was of electrolytic origin, and the cadmium, which contained 0·2 per cent. impurities, was free from iron, arsenic, and antimony. Great care was taken in the casting of the plates to prevent the formation of cracks and blow-holes.

The alloys were annealed at temperatures ascertained from the equilibrium diagram of Jenkins and Hanson * in an electric furnace, which was evacuated to a pressure of 0·01 mm. of mercury. The temperatures of the furnace were measured by means of a copper-nickel nickel-chrome couple, which had been carefully calibrated in the usual manner.

The alloys were slowly heated up to their annealing temperatures, and maintained at within a few degrees of these temperatures for periods of forty-eight hours. After each period of annealing the furnace was slowly cooled to room-temperature, and the resistivities of the alloys measured at room-temperature. This process was repeated until subsequent annealing produced no further change in the resistivities. The alloys were then considered to have reached their final state.

A great deal of attention was paid to annealing, since such accidental factors as casting temperature, rate of cooling, and composition of the mould affect the properties of the alloys. The importance of careful annealing is clearly brought out in the investigation of Jenkins and Hanson † on the Cu–Cd equilibrium diagram. They found from the study of the microstructure of the alloys that the complete γ phase could only be obtained by continuous annealing for eight days. In the present experiments the annealing of the alloys containing from 36 to 44 per cent. of copper was carried on continuously for a week, and altogether for a period of three weeks.

Analysis of the Alloys.

The percentage of copper contained in each alloy was determined by a volumetric method, and the mean of three determinations taken. The percentage of cadmium in each alloy was calculated by difference. The composition and annealing temperatures of the various alloys are given in Table I.

Measurement of Resistance.

The alloy plates were fixed across two knife edges attached to a wooden block supported on an iron base,

* Jenkins and Hanson, *loc. cit.*
† *Loc. cit.*

and the resistance between the knife edges was measured by a Kelvin bridge. The apparatus supporting the plates was contained in an iron box, which could be filled with ice shavings for the determination of the resistance of the plate at 0° C., and through which steam

TABLE I.

Composition and Annealing Temperatures of the Alloys.

Composition of alloys by weight.		Annealing temperatures of the alloys in degrees Centigrade.
Per cent. of copper.	Per cent. of cadmium.	
0·0	100·0	280
1·2	98·8	,,
7·0	93·0	,,
13·3	86·7	,,
16·5	83·5	350
18·0	82·0	,,
18·6	81·4	,,
20·9	79·1	,,
22·8	77·2	,,
24·7	75·3	,,
25·6	74·4	,,
27·9	72·1	450
28·9	71·1	,,
30·5	69·5	,,
31·4	68·6	,,
35·8	64·2	,,
39·3	60·7	,,
42·5	57·5	,,
44·4	55·6	,,
47·7	52·3	,,
54·2	45·8	,,
63·4	36·6	500
78·5	21·5	,,
93·8	6·2	,,
100·0	0·0	,,

could be passed for measurements of resistance at temperatures in the neighbourhood of 100° C.

Satisfactory determinations of the resistivities of the alloys involve accurate measurements of the dimensions of the plates, and it was for this reason that the plates after preparation were rubbed down with emery paper until their dimensions were very nearly uniform. In these measurments special attention was paid to the accurate determination of the thickness of each plate, as this reading involved the greatest possibility of error. The

first set of measurements was carried out with a screw-gauge, and the mean of many readings taken. In the second set of measurements the volume of the plate was accurately determined by weighing it in air and water, and, knowing its area, its thickness could be calculated.

TABLE II.

Resistivities of the Alloys.

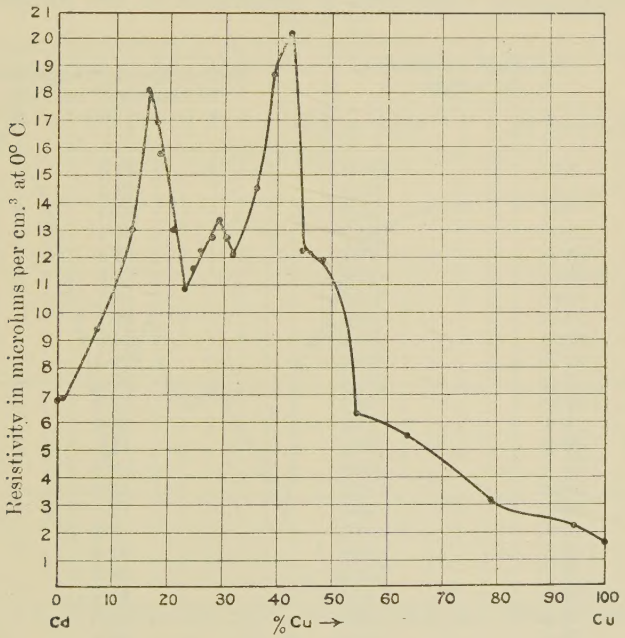
Percentage composition by weight.		Resistivities before annealing in microhms per cm.^{3} at 0° C.	Resistivities after annealing in microhms per cm.^{3} at 0° C.
Per cent. of copper.	Per cent. of cadmium.		
0·0	100·0	6·89	6·83
1·2	98·8	7·05	6·94
7·0	93·0	9·72	9·45
13·3	86·7	12·95	12·99
16·5	83·5	18·24	18·16
18·0	82·0	16·85	16·97
18·6	81·4	15·91	15·85
20·9	79·1	13·32	13·02
22·8	77·2	11·05	10·81
24·7	75·3	11·71	11·60
25·6	74·4	12·28	12·23
27·9	72·1	13·13	12·75
28·9	71·1	13·75	13·38
30·5	69·5	13·20	12·74
31·4	68·6	12·14	12·08
35·8	64·2	13·11	14·57
39·3	60·7	15·31	18·72
42·5	57·5	13·48	20·21
44·4	55·6	12·57	12·25
47·7	52·3	11·56	11·83
54·2	45·8	6·62	6·30
63·4	36·6	5·68	5·45
78·5	21·5	3·21	3·10
93·8	6·2	2·24	2·20
100·0	0·0	1·56	1·56

The values of the thickness of a plate determined by the two methods agreed to within 0·02 per cent.

The presence of serious defects in the plates, such as cracks or blow-holes, could be detected by measuring the resistance of different portions of the plate. Although in nearly all cases the results were very consistent, it was found necessary in a few cases to discard the plates and recast new ones of the same composition. The resistances of all the alloy plates were carefully measured

at the temperature of melting ice, and the resistivities of the alloys of various compositions calculated from the dimensions of the plates. The values of the resistivities of the various alloys in the annealed state at 0° C. are given in Table II., and, taking all factors into consideration, it is estimated that on the average the results are correct to one-third per cent. The results are plotted in Graph I.

GRAPH I.



Temperature Coefficient of Resistance.

The mean temperature coefficients of resistance of the various alloys over the range from 0° C. to about 100° C. were determined by measuring the resistances of the plates at the temperatures of ice and steam respectively. The accuracy of these determinations is not affected by the dimensions of the plates. The values of the temperature coefficients of the annealed alloys are given in Table III., and it is considered that on the average they are correct to within one-half per cent. The results are plotted in Graph II.

Thermoelectric Power of the Alloys.

The thermoelectromotive forces of the alloys were determined with respect to copper leads clamped to the ends of the plates. The ends were jacketed, one being maintained at the temperature of steam, and the other at the temperature of running tap-water. The electro-

TABLE III.

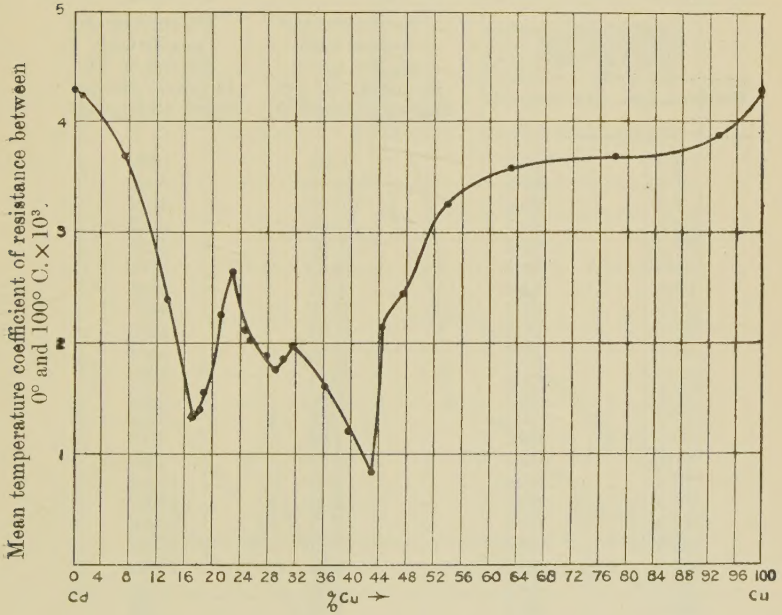
Temperature Coefficient of Resistance of the Alloys.

Percentage composition by weight.		Mean temperature coefficient of resistance between 0° C. and 100° C. × 10^4.
Per cent. Cu.	Per cent. Cd.	
0·0	100·0	42·9
1·2	98·8	42·5
7·0	93·0	37·1
13·3	86·7	24·1
16·5	83·5	13·5
18·0	82·0	13·8
18·6	81·4	15·7
20·9	79·1	22·7
22·8	77·2	26·8
24·7	75·3	21·4
25·6	74·4	20·5
27·9	72·1	19·0
28·9	71·1	17·8
30·5	69·5	18·7
31·4	68·6	19·8
35·8	64·2	15·9
39·3	60·7	12·1
42·5	57·5	8·2
44·4	55·6	21·6
47·7	52·3	24·7
54·2	45·8	32·6
63·4	36·6	35·8
78·5	21·5	37·0
93·8	6·2	39·1
100·0	0·0	43·1

motive forces of the various alloys with respect to the copper wire employed were measured over this range of temperature by means of a Tinsley vernier potentiometer in conjunction with a Weston standard cadmium cell. The mercury thermometer employed in the determination of the temperature of the cold junction was calibrated by comparing its readings with that of an accurate mercury thermometer provided with an N.P.L. certificate. Special experiments were also carried out

to determine whether the thermoelectric powers of the copper-cadmium alloys with respect to the copper wire were constant over the temperature range employed. For this purpose the temperature of the hot junction was varied by passing into the jacket a stream of water of known temperature from a Davis' constant-temperature apparatus. The experimental results showed that the thermoelectric power was constant to within 0·2 per cent. as the temperature range was varied, and it was concluded

GRAPH II.



that the thermoelectromotive force varied linearly with the temperature difference over the range from about 15° C. to 100° C.

As the thermoelectric power had been measured with respect to copper wire, which was not pure, it was decided to measure the thermoelectric power of the latter with respect to copper foil of electrolytic origin, and also with respect to pure lead. The values of the thermoelectric powers of the various alloys with respect to pure copper and pure lead were then determined by applying corrections to the experimental values. The mean

values of the thermoelectric powers of the various alloys with respect to pure copper and pure lead were then plotted with respect to composition, and the results are shown in Graph III. The values are given in Table IV., and it is estimated that, on the average they are correct to one-third per cent.

TABLE IV.

Mean Thermoelectric Power of the Alloys between 10° and 100° C. with respect to pure Lead and pure Copper.

Composition of alloy by weight.		Thermoelectric power with respect to Cu in microvolts per degree Centigrade.	Thermoelectric power with respect to Pb in microvolts per degree Centigrade.
Per cent. Cu.	Per cent. Cd.		
0·0	100·0	1·69	4·84
1·2	98·8	1·78	4·93
7·0	93·0	0·37	3·52
13·3	86·7	— 1·03	2·12
16·5	83·5	— 1·65	1·50
18·0	82·0	— 0·41	2·74
18·6	81·4	— 0·37	2·78
20·9	79·1	0·82	3·97
22·8	77·2	1·41	4·66
24·7	75·3	— 1·73	1·42
25·6	74·4	— 2·24	0·91
27·9	72·1	— 2·85	0·30
28·9	71·1	— 3·28	— 0·13
30·5	69·5	— 2·03	1·12
31·4	68·6	— 0·47	2·68
35·8	64·2	9·98	13·13
39·3	60·7	13·42	16·57
42·5	57·5	17·71	20·86
44·4	55·6	11·89	15·04
47·7	52·3	10·80	13·95
54·2	45·8	5·02	8·17
63·4	36·6	4·32	7·47
78·5	21·5	1·72	4·87
93·8	6·2	0·23	3·38
100·0	0	0·00	3·15

The Hall Effect of the Alloys.

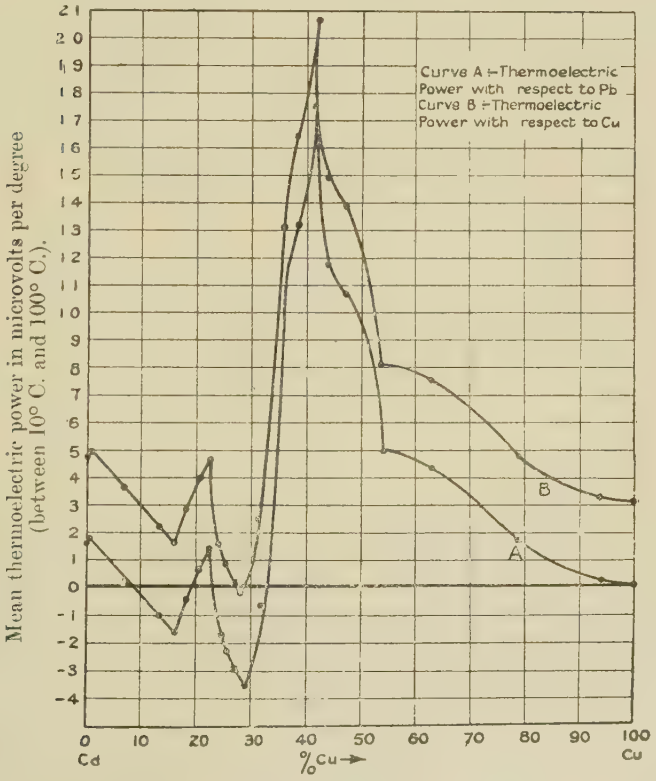
When a metal plate conveying an electric current is placed in a magnetic field so that the lines of force are normal to the conducting plate and to the direction of flow of the electric current a transverse galvano-magnetic potential difference, known as the Hall effect, is set up between the edges of the plate.

It has been experimentally proved that for a given metal the Hall potential difference is given by the formula

$$E = \frac{R.H.I}{d},$$

where H is the magnetic field in gauss, I the current in absolute units, d the thickness of the plate in centimetres, and R the Hall coefficient.

Graph III.



The coefficient R depends on the temperature, and for some metals on the intensity of the magnetic field as well.

According to Ettingshausen and Nernst * the magnitude of the Hall coefficient depends to a certain extent on the length of the plates. They found during their investigations of the Hall effect in bismuth that the effect was less

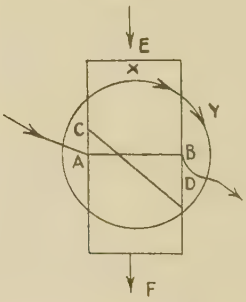
* *Zeit. Phys. Chem.* ii. p. 104 (1888).

in short plates, and advocated the use of plates in which the ratio of the length to the breadth was at least 3 : 2. In the present investigation of the Hall coefficients of the copper-cadmium alloys the ratio of the length to the breadth of each plate was 5 : 1.

The Hall effect may be positive or negative, the sign differing for various metals. The convention can be readily understood from the following diagram (fig. 2) :—

The rectangle X represents the plate, and the circle Y with the arrowheads indicating the direction of the current in the electromagnet represents the magnetic field. The direction of the primary current is given by EF, the position of the equipotential line before the application of the field by AB, and the position of this equipotential

Fig. 2.



line when the field is applied by CD. If the equipotential line AB is rotated in the direction of the current in the electromagnet the effect is said to be positive, and if the equipotential line is rotated in the opposite direction the effect is said to be negative. In the present experiments the sign of the effect is found by comparison with a plate of electrolytic copper. The Hall coefficients of both copper and cadmium are small and of opposite sign, the coefficient of copper being negative and of cadmium positive. The sign of the coefficient of the intervening alloys are either positive or negative, according to the composition.

Since the Hall coefficients are small a very sensitive Paschen galvanometer was used to measure them. The galvanometer was protected from external fields by a double shield of soft iron. The instrument was mounted

on a concrete pillar built into the foundations of the laboratory and situated at a distance of about 8 metres from the powerful circular electromagnet, which had been rotated into such a position that its effect on the galvanometer was at a minimum. The pole pieces of the electromagnet were of circular cross-section, having a diameter of 9 cm., and the magnetic field between them was practically uniform over the air-gap of 1·5 cm.

The alloy under investigation was rigidly fixed in an upright wooden stand between the poles of the magnet by means of two brass clamps, which also served as leads for the plate current. The wooden frame also carried two secondary electrodes consisting of spring metallic contacts mounted on ebonite supports.

The secondary electrodes could be moved along the edges of the plate by means of two fine screws, and were connected to the galvanometer by means of well insulated flexible leads of measured resistance. Experience showed that very minute movements of the flexible leads, due to air currents and accidental vibrations, produced small induced currents in the delicate Paschen galvanometer, and, as a consequence, it was necessary to keep the leads as taut as possible, especially the portion near the electromagnet.

In order to measure the Hall potential difference it was first necessary to set the secondary electrodes along an equipotential line. This was accomplished by adjusting the screws controlling the movement of the secondary electrodes until on reversing the current through the plate no deflexion of the galvanometer was produced. When the electromagnet was excited and the secondary circuit closed a deflexion was produced in the galvanometer due to the Hall potential difference between the edges of the plate. After the spot of light had come to rest the deflexion on reversal of the plate current was taken and recorded. The plate current was reversed several times, and the mean value of the deflexion taken. This reversal of the plate current eliminated any error in the setting of the secondary electrodes on an equipotential line, and also the potential difference set up at the edges of the plate, if there is a flow of heat in a given direction along the plate (Nernst effect). The galvanometer circuit was then broken, and after the magnetic field had been reversed a second series of readings was

obtained. The field was then re-established in its original direction, and the procedure described above was repeated. The mean of the four sets of observations was taken, the galvanometer having been calibrated before and after each set.

The calibration was effected by applying a known potential difference across the galvanometer terminals and measuring the resulting deflexion. The resistances employed in these experiments had been calibrated. From a knowledge of the resistances of the leads and galvanometer it was then possible to calculate the potential difference between the edges of the plate corresponding to the galvanometer deflexion due to a field of known strength. The maximum field employed in these experiments was 8500 gauss, which corresponded to a current of 6 amperes passing through the electromagnet coils.

The Hall potential difference was measured for various magnetic fields, and in the case of each alloy a linear relation connecting the potential difference and field was obtained. The constant value of $\frac{E}{H}$ was read off from a graph, an example of which for the alloy containing 16·5 per cent. copper is given in fig. 3. The value of R, the Hall coefficient, could then be calculated from

$$R = \frac{Ed}{HI}.$$

A primary current of 4 amperes was employed throughout this investigation, and it could be read to 1 part in 1200 on a delicate Weston ammeter.

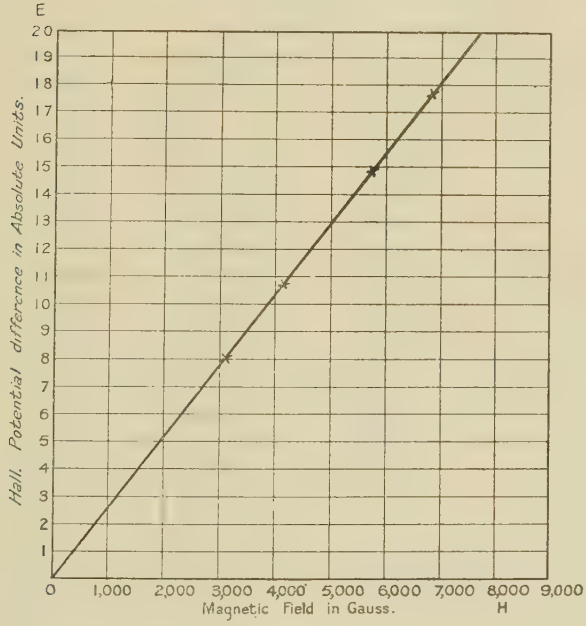
The absolute value of the magnetic field, corresponding to a current of 2 amperes passing through the electromagnet coils, was determined in the usual manner by means of a search coil of known mean area and a delicate ballistic galvanometer.

The intensities of the magnetic fields corresponding to other currents passing through the coils of the electromagnet had previously been determined by means of a search coil and Grassot fluxmeter, and by making use of the ballistic galvanometer determination the various fluxmeter values could be corrected.

The accuracy of the measurement of the field was further tested by measuring the Hall coefficient of pure copper,

and comparing the results obtained with those of other observers. The result of this comparison was satisfactory, the value obtained in these experiments being —·000523, and the mean value found by other observers under the same conditions being —·000520 *. It is estimated that the magnetic fields have been determined correctly to within 1 in 200. The values of the Hall coefficients were measured at room-temperatures, the actual tempera-

Fig. 3.



ture being read from a thermometer suspended near the plate.

It is important to note that, in addition to the Hall effect, a transverse galvanomagnetic temperature difference is set up between the edges of the plate; this is the Ettingshausen effect, whose magnitude is usually very small. The difference in temperature dT is given by $d\mathrm{T} = \frac{\mathrm{P.H.I}}{d}$, where H is the magnetic field in absolute

* Campbell, 'Galvanomagnetic and Thermomagnetic Effects,' p. 121.

units, I the current in absolute units, d the thickness of the plate in cms., and P the Ettingshausen coefficient.

The Hall and Ettingshausen effects are superposed, and unless the secondary electrodes are of the same material as the plate itself the Ettingshausen temperature difference dT set up between the edges of the plate

TABLE V.

The Hall Coefficient of the Alloys.

Percentage composition by weight.		Hall coefficient	Temperature
Per cent. of copper.	Per cent. of cadmium.	$\times 10^{1}$.	in ° C.
0·0	100·0	+ 5·30	16·8
1·2	98·8	+ 5·41	16·7
7·0	93·0	+ 1·52	15·5
13·3	86·7	−13·79	15·5
16·5	83·5	−19·61	13·2
18·0	82·0	−14·54	13·6
18·6	81·4	−13·88	13·8
20·9	79·1	− 9·86	14·2
22·8	77·2	− 8·14	14·3
24·7	75·3	− 6·50	15·4
25·6	74·4	− 6·01	15·3
27·9	72·1	− 5·43	15·0
28·9	71·1	− 4·48	14·8
30·5	69·5	− 6·83	14·9
31·4	68·6	− 9·90	12·7
35·8	64·2	− 3·21	12·7
39·3	60·7	+ 4·22	13·1
42·5	57·5	+ 7·79	13·8
44·4	55·6	−12·80	14·0
47·7	52·3	−14·02	15·1
54·2	45·8	−12·11	15·6
63·4	36·6	− 8·95	15·3
78·5	21·5	− 4·67	15·4
93·8	6·2	− 3·65	15·5
100·0	0·0	− 5·23	15·2

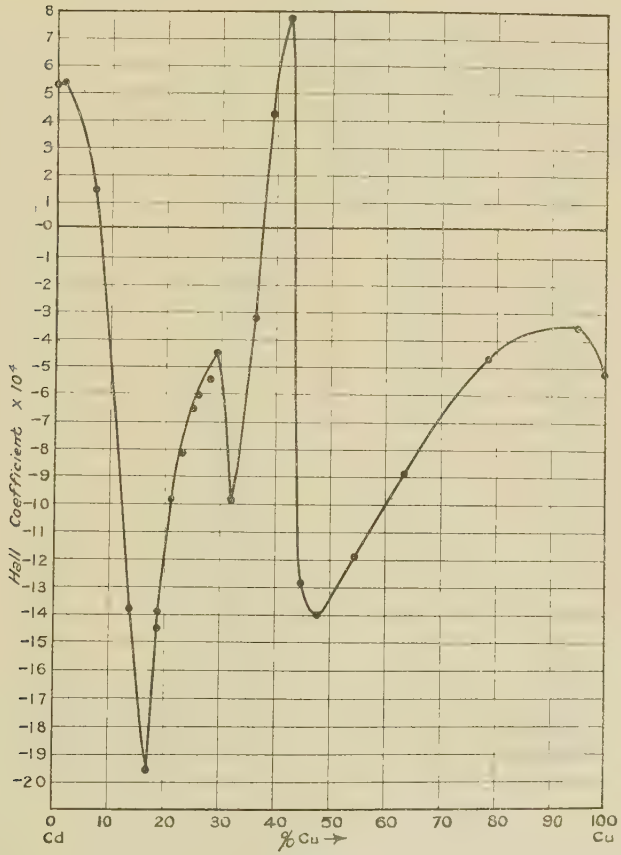
produces an electromotive force $\theta\, d$T, where θ is the thermoelectric power of the electrode with respect to the plate.

Hence the observed value for the potential difference is given by $E = E_H \pm \theta\, d$T, where E_H is the true potential difference due to the Hall effect. Then R, the Hall coefficient, becomes

$$R = \frac{E_H . d}{H . I} \pm P\theta.$$

The values of P are generally very small, and depend on the nature of the metal. There is comparatively little data relating to the magnitude of this coefficient for alloys, but its values for the constituent metals of the binary system examined in these experiments are very

GRAPH IV.



small, being $-1{\cdot}69\times10^{-9}$ and $-2{\cdot}89\times10^{-9}$ for copper and cadmium respectively. It is important, however, to remember that the magnitude of the potential difference also depends on the thermoelectric power of the electrode with respect to the plate.

Determinations of the Hall coefficients were made, using

secondary electrodes of copper and aluminium, and the values obtained were the same in each case. The Ettingshausen effect also takes time to reach its full value, but in these experiments there was no gradual creep in the observed deflexions during measurements of the Hall potential difference. Hence no correction for the Ettingshausen effect was necessary.

Table VI.

The Densities of the Alloys.

Percentage composition by weight.		Density in grams per c.c.	Temperature in 0° C.
Per cent. of copper.	Per cent. of cadmium.		
0·0	100·0	8·631	14·8
1·2	98·8	8·635	14·8
7·0	93·0	8·694	14·9
13·3	86·7	8·783	14·7
16·5	83·5	8·836	15·4
18·0	82·0	8·832	15·4
18·6	81·4	8·839	15·4
20·9	79·1	8·815	15·4
22·8	77·2	8·819	15·7
24·6	75·4	9·003	15·6
25·7	74·3	9·021	15·8
27·7	72·3	9·054	13·9
28·9	71·1	9·085	14·2
30·5	69·5	9·092	14·2
31·4	68·6	9·090	14·1
35·8	64·2	9·044	14·1
39·3	60·7	9·015	14·1
42·5	57·5	8·875	15·3
44·4	55·6	8·879	15·2
47·7	52·3	8·891	15·0
54·2	45·8	8·937	15·5
63·4	36·6	8·924	15·3
78·5	21·5	8·851	15·3
93·8	6·2	8·875	14·4
100·0	0·0	8·932	14·5

The values of the Hall coefficients for the various alloys are given in Table V. and plotted in Graph IV.

It is estimated, from a consideration of the various factors involved, that the determinations of the Hall coefficients are correct to within 1 per cent.

Densities of the Alloys.

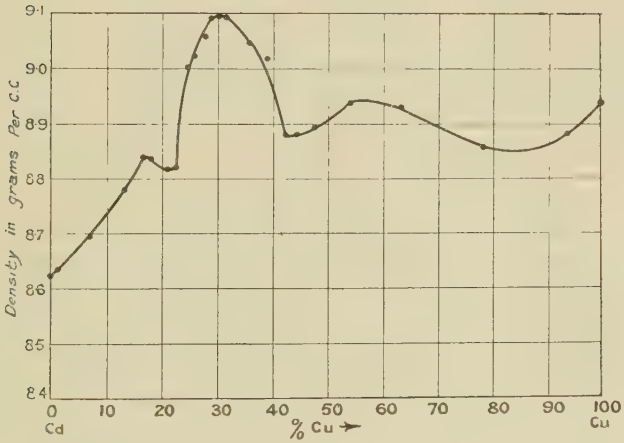
The alloys were weighed in air and in pure distilled water at a known temperature. The density of the water

being known, the volumes of the plates could be determined and their densities calculated. The results are given in Table VI. and plotted in Graph V. It is considered that the densities have been determined with an error of not more than 0·1 per cent.

Specific Heats of the Alloys.

The specific heats of the alloys were determined by means of a Joly steam calorimeter in the usual manner. The thermometer employed in these experiments had been calibrated by comparison with a standard thermometer.

GRAPH V.



The mean specific heats between 18·5° C. and 100° C. are collected in Table VII. and plotted in Graph VI. It is estimated that the results are accurate to within 1 per cent. on the average.

Discussion of Results.

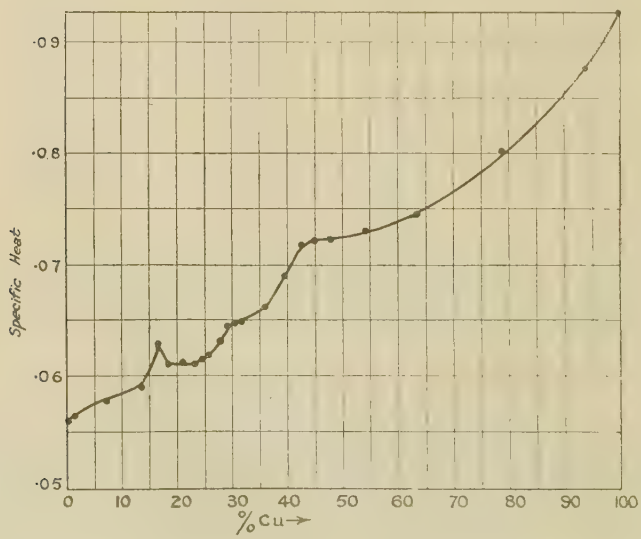
The investigation of the electrical properties of an alloy system is a powerful method of detecting changes of phase, and the results obtained are generally in good agreement with those obtained by thermal methods. The variation of physical properties of the alloys with composition will therefore be examined for phase changes, and the results considered in relation to the equilibrium diagram.

TABLE VII.

The Mean Specific Heats of the Alloys between 18·5° C. and 100° C.

Percentage composition by weight.		Mean specific heat between	Percentage composition by weight.		Mean specific heat between
Per cent. Cu.	Per cent. Cd.	18·5° and 100° C.	Per cent. Cu.	Per cent. Cd.	18·5° and 100° C.
0·0	100·0	·0559	28·9	71·1	·0647
1·2	98·8	·0563	30·5	69·5	·0648
7·0	93·0	·0578	31·4	68·6	·0650
13·3	86·7	·0590	35·8	64·2	·0663
16·5	83·5	·0630	39·3	60·7	·0691
18·0	82·0	·0607	42·5	57·5	·0718
18·6	81·4	·0611	44·4	55·6	·0724
20·9	79·1	·0613	47·7	52·3	·0723
22·8	77·2	·0610	54·2	45·8	·0732
24·7	75·3	·0614	63·4	36·6	·0746
25·6	74·4	·0618	78·5	21·5	·0805
27·9	72·1	·0633	93·8	6·2	·0880
			100·0	0·0	·0934

GRAPH VI.



The curves showing the relation between the various electrical properties and composition show discontinuities near all or some of the points corresponding to $CuCd_3$,

Cu_2Cd_3, Cu_4Cd_3, and Cu_2Cd. These are the compounds given by Jenkins and Hanson * as the result of their investigation of the thermal properties of the alloys. At the copper end of the series the resistivity (Graph I.) at first increases gradually with addition of cadmium until the alloy containing 54·2 per cent. of copper is reached, then more rapidly to a maximum for the alloy containing 42·5 per cent. of copper. The resistivity of this alloy is 20·21 microhms per cm.^{3}, and is about fourteen times that of copper and three times greater than that of cadmium.

At the other end of the series the addition of copper to cadmium causes at first a measurable increase in the resistivity over the small range from pure cadmium to 1·2 per cent copper, and afterwards a much more rapid increase to a maximum value of 18·16 microhms per cm.^{3} near the composition of the compound $CuCd_3$, which contains 15·9 per cent. of copper. This change in the slope of the resistivity curve is due to the introduction of the ϵ phase.

With the introduction of the δ constituent at the composition corresponding to about 16·5 per cent. of copper the resistivity decreases, and reaches a minimum at the composition 22·8 per cent. of copper, which roughly coincides with the boundary of the δ and $(\delta+\epsilon)$ phases. At this point the ϵ phase disappears, and the resistivity curve rises to a second maximum at the composition 28·9 per cent. of copper, which corresponds approximately to the compound Cu_2Cd_3 †.

This maximum is followed by a second minimum which occurs near the boundary of the δ and $(\gamma+\delta)$ phase, at a composition corresponding to 31·4 per cent. of copper. On entering the $(\gamma+\delta)$ phase there is a rapid increase in the resistivity, which reaches its maximum value at the composition 42·5 per cent. of copper, which corresponds to the compound Cu_4Cd_3.

The curve shows no more well-defined singular points, but distinct discontinuities or points of inflexion occur

* *Loc. cit.*

† In the graphs connecting the electrical properties of the various alloys with composition, slight kinks corresponding to 27·9 per cent. copper have been smoothed out. These kinks may correspond to the compound Cu_2Cu_3 (27·4 per cent. copper), and the next point of inflexion at 28·9 per cent. copper is very near to the boundary δ and $\gamma+\delta$ phases as determined by Jenkins and Hanson.

at compositions corresponding to 44·4 and 54·2 per cent. of copper. The former composition corresponds to the boundary of the γ and the $(\beta+\gamma)$ phases and the latter to the compound Cu_2Cd, which is at the boundary between the $(\beta+\gamma)$ and the $(\alpha+\beta)$ phases. Apart from the former discontinuity the introduction of the β constituent does not materially alter the form of the resistivity-composition curve. Except at the two ends of the series (pure copper and pure cadmium) no data seems available for comparison with the results of the present investigation. However, the value of the resistivity obtained for copper ($1{\cdot}561\times10^{-6}$ ohms per cm.^{3} at 0° C.) is in good agreement with that given in the International Critical Tables, and the value obtained for cadmium ($6{\cdot}83\times10^{-6}$ ohms per cm.^{3} at 0° C.) with that ($6{\cdot}828\times10^{-6}$) determined by Lees *.

The resistivities of the various alloys were not in general much affected by annealing except in the region extending from 36 to 44 per cent. of copper. In this region, as shown by an examination of Table II., large changes in the resistivities occurred. In the case of the alloy containing 42·5 per cent. of copper annealing produced an increase of 50 per cent. in the resistivity. According to the equilibrium diagram it will be seen that the region corresponds to the $(\gamma+\delta)$ and γ phases, and Jenkins and Hanson found that in order to separate out the complete γ constituent it was necessary to anneal for a considerable time at a temperature of 450° C. Annealing therefore causes a separation of the γ phase, and this explains the changes in the resistivities of the alloys in the region considered.

The mean temperature coefficient of resistance is also very sensitive to changes of phase, as shown by Graph II. No discontinuity occurs at the eutectic point (1·2 per cent. copper), and the mean temperature coefficient decreases continuously with increase of copper content to about the value $1{\cdot}35\times10^{-3}$ for the compound $CuCd_3$, which contains 15·9 per cent. of copper. On the introduction of the δ phase at the above composition the temperature coefficient increases rapidly to a maximum at the composition (22·8 per cent. Cu) which nearly corresponds to the boundary between the δ and $(\delta+\epsilon)$ phases. With

* Phil. Trans. ccviii. p. 381 (1908).

further increase of copper content the temperature coefficient again decreases and reaches a second minimum near the compound Cu_2Cd_3, which contains 27·4 per cent. of copper. The boundary of the δ and $(\gamma+\delta)$ phases is shown by the maximum at the composition corresponding to 31·4 per cent. copper. Near this point the γ phase enters and a diminution occurs in the temperature coefficient, which reaches a minimum value for the compound Cu_4Cd_3, which contains 42·9 per cent. of copper. A further discontinuity occurs at the composition (44·4 per cent. copper), which corresponds to the boundary between the γ and the $(\gamma+\beta)$ phases. There is, however, no definite evidence in this case for the existence of the compound Cu_2Cd.

The graph (Graph III.) showing the relation between the thermoelectric power of the alloys with respect to both lead and copper, and the composition of the alloys, also show discontinuities at compositions corresponding to those of the four compounds. The various phase changes indicated by the equilibrium diagram are also shown as discontinuities on the graphs. It is interesting to note that the thermoelectric power graph for the alloy-copper junctions crosses the composition axis at the four points corresponding to 9, 19, 23, and 32·0 per cent. copper. These changes in the sign of the thermoelectric power are intimately connected with the phase changes indicated in the equilibrium diagram.

The Hall effect of the alloys is also very sensitive to phase changes. Graph IV., giving the relation between the Hall coefficients of the alloys and their composition, shows discontinuities at points corresponding to the compounds $CuCd_3$, Cu_2Cd_3, and Cu_4Cd_3, but no discontinuity at the point corresponding to the compound Cu_2Cd. The curve also shows discontinuities corresponding to all phase changes with the exception of the passage through the boundary between the δ and the $(\delta+\epsilon)$ phases. It is of interest to note that the Hall coefficients of alloys containing about 8, 37, and 43 per cent. of copper are zero. No satisfactory explanation of a zero Hall coefficient is available on present theories. From the nature of the graph it is evident that the Hall coefficient is intimately connected with the structure of the various alloys. The Hall coefficient is independent of the magnetic

field strength for all the alloys examined in this investigation.

Although the curves showing the relation between the various electrical properties and composition show many points of resemblance, it does not seem possible to draw general conclusions connecting the relative variations of these properties.

Density and specific heat are far less sensitive to changes in composition than the other physical properties investigated. In Graphs V. and VI., showing the variation of density and specific heat with composition, breaks occur at points corresponding to some of the four compounds, but they are not nearly as well defined as the marked singular points which occur in the graphs of the other physical properties. The most definite singular point in the above graphs is the one corresponding to the compound Cd_3Cu (15·9 per cent. Cu) in the specific heat graph.

Summary.

(1) The electrical resistivities, temperature coefficients of resistance, thermoelectric powers, Hall coefficients, and the specific heats and densities of the copper-cadmium series of alloys have been determined.

(2) The alloys were cast in graphite moulds in the form of plates, and their electrical resistivities at the temperature of melting ice were determined. The plates were then annealed for long periods at suitable temperatures until further annealing produced no change in their resistivities. The Hall coefficient and other physical properties were then determined in the final state.

(3) The curves giving the relation between the electrical properties and the composition of the alloys show in general singular points at compositions near those of the compounds $CuCd_3$, Cu_2Cd_3, Cu_4Cd_3, and Cu_2Cd. The presence of a compound at the composition corresponding to Cu_2Cd is not, however, indicated by the graphs showing the relation between composition of the alloy and (*a*) the Hall effect and (*b*) the temperature coefficient of resistance.

The discontinuities were much less pronounced at the points corresponding to the compositions of the above compounds in the density and the specific heat graphs.

(4) The variations of the resistivities and the thermoelectric powers of the alloys with composition were accompanied by variations in the Hall effect, and the

corresponding graphs show many points of similarity. A study of these graphs in relation to the equilibrium diagram shows that the variations in the electrical properties follow the changes of phase of the system.

(5) Annealing produced little effect on the electrical resistivity except in the region containing from 36 to 44 per cent. of copper. The comparatively large changes in resistivities of alloys in the above region produced by annealing is due, as pointed out by Jenkins and Hanson, to the separation of the γ phase.

XVII. *Kinetics of a Catalysed Isomeric Change in Solution.*

By R. C. Traill, *Ph.D.**

THE work of Hinshelwood and others has established the concept of kinetic activation in chemical reactions in the gaseous phase. According to this, of the total number of collisions between molecules of the reactants, the fraction which produces a chemical reaction is given by the probability that there will be available between two colliding molecules energy greater than a certain minimum, which is the energy of activation. According to Lewis †, the velocity-coefficient of a bimolecular gaseous reaction is given (in gram molecules per litre, and minutes) by the equation

$$k = 114 \times 10^{21} \times \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \times \sqrt{u_1^2 + u_2^2} \times e^{-E/RT},$$

where σ_1, σ_2 are the diameters, u_1, u_2 are the mean velocities (in cm. per sec.) of the reacting molecules, and E is the energy of activation calculated from the temperature coefficient of the reaction.

The applicability of this equation to a reaction in solution was tested by Norrish and Smith ‡, who introduced a correcting term to allow for the volume occupied by the solvent molecules. They investigated the reaction between trimethylamine and *m*- or *p*-nitrobenzyl chloride in benzene solution, and found a large discrepancy between the velocity-coefficient as calculated in the above manner, and that observed experimentally. The probability factor, P, being

* Communicated by T. M. Lowry, C.B.E., M.A., D.Sc., F.R.S.

† Journ. Chem. Soc. cxiii. p. 471 (1918).

‡ Journ. Chem. Soc. p. 129 (1928).

the ratio of the observed to the calculated velocity, was 2×10^{-8} for this reaction, and varied from 5×10^{-5} to 4×10^{-11} for a number of other reactions tabulated by them. They concluded that the discrepancy was due to deactivation by solvent molecules, to an extent characteristic of both the reactants and the solvent.

In the present paper some recent measurements of the velocity of catalysed mutarotation of beryllium benzylcamphor in carbon tetrachloride and in chloroform * have been analysed on the basis of the law of Mass Action, in order to provide data for investigating the applicability of Lewis's equation to this reaction. As a result of these calculations the velocity-coefficients deduced from Lewis's equation have been found to be of the same order of magnitude as those observed experimentally, the differences being within the uncertainty of calculation. In these very simple changes, therefore, practically every collision between reactant molecules with sufficient energy is effective, as contrasted with the extremely small probabilities in reactions involving the ionization of one of the components.

Application of the Law of Mass Action to a Catalysed Isomeric Change.

It is assumed that the isomeric change between the two forms, B_α and B_β, of beryllium benzoylcamphor can take place only through combination with the catalyst, A, to form a complex AB_α or AB_β. The change may then be formulated in three steps:

$$\text{(i.)} \quad B_\alpha + A \rightleftharpoons AB_\alpha,$$
$$\text{(ii.)} \quad AB_\alpha \rightleftharpoons AB_\beta,$$
$$\text{(iii.)} \quad AB_\beta \rightleftharpoons B_\beta + A.$$

If reactions (i.) and (iii.) are fast compared with (ii.) they will be in equilibrium throughout the mutarotation and

$$[AB_\alpha] = q_\alpha[A][B_\alpha]$$
$$[AB_\beta] = q_\beta[A][B_\beta].$$

As a simplification we may take $q_\alpha = q_\beta = q$.

The velocity of change at any moment is given by

$$\frac{dx}{dt} = k_1'[AB_\alpha] - k_2'[AB_\beta].$$

* Lowry and Traill, Proc. Roy. Soc.

If a be the total concentration of catalyst,

b be the total concentration of beryllium benzylcamphor, it can be shown that

$$k = \frac{k'}{2bq}\left\{(aq+bq+1)-\sqrt{(aq+bq+1)^2-4abq^2}\right\}, \quad (1)$$

where k is the observed velocity-coefficient of the reaction, and $k' = k_1' + k_2'$.

If [AB] is negligible in comparison with a, this relation can be obtained in a simpler form,

$$k = k'\frac{aq}{1+aq} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

TABLE I.

Catalysis by Pyridine in Carbon Tetrachloride.

20°. $k'' = 0{\cdot}132.$			25°. $k'' = 0{\cdot}227.$			30°. $k'' = 0{\cdot}385.$		
a	k(obs.).	k(calc.).	a.	k(obs.).	k(calc.).	a	(k(obs.).	k(calc.).
0·519	0·0695	0·0683	0·130	0·0322	0·0294	0·130	0·0500	0·0500
0·839	0·109	0·110	0·209	0·0535	0·0475	0·259	0·101	0·100
			0·511	0·119	0·116	0·387	0·148	0·149
			0·773	0·162	0·175			
			0·993	0·226	0·225			
			1·048	0·238	0·238			

Finally, if q be extremely small, so that aq is negligible in comparison with unity, equation (2) reduces to

$$k = k'aq = k''a \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $k'' = k'q$ is a constant catalytic coefficient, or bimolecular velocity-coefficient for the reaction.

The results obtained for the rate of mutarotation of beryllium benzoylcamphor in carbon tetrachloride when catalysed by pyridine conform to equation (3), and are shown, together with the constants deduced, in Table I.

The results obtained with alcohol as catalyst conform to equation (1). Values of k', the unimolecular velocity-coefficient of the isomeric change of the complex, and of q, the mass action constant, chosen to fit the results best, are shown, together with the experimental figures, in Table II.

Similar results were obtained with *p*-cresol as catalyst, and are shown in Table III. The agreement here is not, however, so good, especially at low catalyst concentration, and it is possible that the effect of *p*-cresol is not so simple.

TABLE II.

Catalysis by Alcohol in Carbon Tetrachloride.

20°.				25°.				30°.			
$k' = 0{\cdot}105$.				$k' = 0{\cdot}185$.				$k' = 0{\cdot}329$.			
$q = 2{\cdot}2$.				$q = 2{\cdot}0$.				$q = 2{\cdot}0$.			
b.	*a*.	*k*(obs.).	*k*(calc.).	*b*.	*a*.	*k*(obs.).	*k*(calc.).	*b*.	*a*.	*k*(obs.).	*k*(calc.).
0·042	0·289	0·0395	0·0394	0·077	0·0037	0·0014	0·0012	0·038	0 142	0·0696	0·0695
0·037	0·710	0·0634	0·0632	0·075	0·0307	0·0092	0·0094	0·039	0·289	0·116	0·117
0·038	1·434	0·0790	0·0793	0·082	0·0450	0·0116	0·0134	0·042	0·431	0·150	0·149
				0·085	0·107	0·0320	0·0292				
				0·092	0·290	0·065	0·063				
				0·080	0·576	0·094	0·095				
				0·084	0·859	0·114	0·114				
				0·081	1·146	0·127	0·126				

TABLE III.

Catalysis by *p*-cresol in Carbon Tetrachloride at 25°.

$k' = 0{\cdot}127$. $q = 2{\cdot}5$.

b.	*a*.	*k*(obs.).	*k*(calc.).
0·037	0·0356	0·0060	0·0096
0·037	0·0501	0·0081	0·0132
0·037	0·0540	0·0118	0·0151
0·033	0·100	0·0175	0·0257
0·036	0·110	0·0275	0·0275
0·037	0·244	0·0525	0·0483
0·037	0·358	0·0627	0·0601
0·037	0·586	0·0741	0·0756
0·037	1·18	0·0961	0·0952

Influence of the Solvent.

The isomeric change of beryllium benzoylcamphor in chloroform proceeds to an equilibrium which is different from that in carbon tetrachloride. It has been shown * that

* Burgess and Lowry, Journ. Chem. Soc. cxxv. p. 2081 (1924).

beryllium benzoylcamphor combines with two molecular proportions of chloroform to give a crystalline compound, the properties of which suggest that it contains equimolecular proportions of the α and β forms. It is therefore formulated as a "racemate," $B_\alpha B_\beta, 4CHCl_3$. The change of equilibrium in chloroform is then easily accounted for by a difference of stability of two isomeric chloroform complexes, $B_\alpha, 2CHCl_3$ and $B_\beta, 2CHCl_3$. These complexes are assumed to undergo isomeric change only when the chloroform has been displaced by an active catalyst such as alcohol or pyridine.

In addition to the reactions (i.), (ii.), and (iii.) (p. 226), we now write

$$\text{(iv.)} \quad B_\alpha + 2S \rightleftharpoons B_\alpha S_2,$$

$$\text{(v.)} \quad B_\beta + 2S \rightleftharpoons B_\beta S_2,$$

where S is a molecule of the solvent. If these reactions, like (i.) and (iii.), are fast compared with (ii.), they will be in equilibrium throughout, and

$$[B_\alpha S_2] = p_\alpha [B\ ][S]^2$$

$$[B_\beta S_2] = p_\beta [B_\beta][S]^2,$$

where p_α, p_β are mass action constants for the respective forms. The velocity-coefficient k_c in chloroform is now given by the equation

$$k_c = [A]q \left\{ \frac{k_{c_1}'}{1 + [A]q + p_\alpha [S]^2} + \frac{k_{c_2}'}{1 + [A]q + p_\beta [S]^2} \right\}. \quad (4)$$

If $[A]q$ is small, this reduces to

$$\left.\begin{aligned} k_c &= aq \left\{ \frac{k_{c_1}'}{1 + p_\alpha [S]^2} + \frac{k_{c_2}'}{1 + p_\beta [S]^2} \right\} \\ &= ak_c'' \end{aligned}\right\}. \quad (5)$$

If the ratios of the total α form to the total β form of beryllium benzoylcamphor present at equilibrium in carbon tetrachloride and chloroform be r and r_c respectively, then, for the above condition,

$$r = \frac{k_2''}{k_1''}, \quad (6)$$

and

$$r_c = \frac{k_2''}{k_1''} \frac{1 + p_\alpha [S]^2}{1 + p_\beta [S]^2} = r \frac{1 + p_\alpha [S]^2}{1 + p_\beta [S]^2}. \quad (7)$$

It may further be shown that

$$p_\alpha[\mathrm{S}]^2 = \frac{(1+r_c)k''}{(1+r)k_c''} - 1. \quad . \quad . \quad . \quad . \quad (8)$$

$$p_\beta[\mathrm{S}]^2 = \frac{(1+r_c)rk''}{(1+r)r_c k_c''} - 1. \quad . \quad . \quad . \quad . \quad (9)$$

which give p_α, p_β in terms of determinable quantities.

The experimental values obtained with pyridine in chloroform are shown in Table IV.

Inserting the values $r = \frac{0{\cdot}51}{0{\cdot}49} = 1{\cdot}04$, $r_c = \frac{0{\cdot}41}{0{\cdot}59} = 0{\cdot}70$ $k''/k_c'' = 2{\cdot}27$ in equations (8) and (9), the mass action constants are found to be

$$p_\alpha = 0{\cdot}0058 \qquad p_\beta = 0.0116.$$

TABLE IV.

Catalysis by Pyridine in Chloroform at 25°.

$k_c'' = 0{\cdot}100$.

a.	k(obs.).	k(calc.).
0·260	0·0276	0·0260
0·642	0·0604	0·0642
0·902	0·0906	0·0902

The constants imply that, at the molecular concentration, 12·4, of pure chloroform, 46 per cent. of the α form and 64 per cent. of the β form is combined with the solvent.

Equation (4) can be obtained as

$$k_c = \frac{k_c'[\mathrm{A}]q}{1+r}\left\{\frac{1}{1+[\mathrm{A}]q+p_\alpha[\mathrm{S}]^2} + \frac{r}{1+[\mathrm{A}]q+p_\beta[\mathrm{S}]^2}\right\}, \quad . \quad . \quad . \quad . \quad (10)$$

where all the quantities on the right side have been determined except [A] and k_c'. Since in the experiments a is usually substantially greater than b, it is possible, by estimating [AB] approximately, to obtain values of [A] from the relation

$$[\mathrm{A}] = a = [\mathrm{AB}],$$

without introducing appreciable error. Further, by making use of the relation $k_c' = 1{\cdot}24\,k'$, which can be deduced theoretically from the rate of collision of the solvent molecules with those of the complex (see p. 233), the velocity of

mutarotation of beryllium benzoylcamphor in chloroform, when catalysed by alcohol or cresol, can be predicted. The nature of the agreement is shown in Tables V. and VI. It will be seen that there is good agreement between theory and experiment in the case of alcohol, but that the calculated values for cresol are some 50 per cent. too high. This

TABLE V.

Catalysis by Alcohol in Chloroform at 25°.

b.	*a*.	*k*(obs.).	*k*(calc.).
0·042	0·179	0·0273	0·0300
0·038	0·358	0·0492	0·0520
0·040	0·534	0·0683	0·0730
0·040	0·712	0·0871	0·0875
0·041	1·068	0·113	0·111
0·041	1·408	0·128	0·129

TABLE VI.

Catalysis by *p*-Cresol in Chloroform at 25°.

b.	*a*.	*k*(obs.).	*k*(calc.).
0·037	0·410	0·0294	0·0465
0·035	0·819	0·0496	0·0755
0·032	1·289	0·0692	0·0970

TABLE VII.

Catalyst.	$k_{30°}/k_{20°}$.	E.
(*a*) Pyridine	2·92	18,900 cal.
(*b*) Alcohol	3·14	20,200 ,,

divergence is of the same order as that for the lower concentrations of cresol in carbon tetrachloride, and may be due to a common cause ; or is perhaps a result of association of the molecules of *p*-cresol itself.

Application of the Theory of Kinetic Activation.

The energy of activation for the isomeric change, when catalysed by pyridine and by alcohol, can be calculated from the temperature-coefficient in the usual way, and the results are shown in Table VII.

The value for pyridine is obtained from k'' of equation (3), which is a bimolecular velocity-coefficient. The velocity of isomeric change is therefore proportional to the rate of collision of the reacting molecules and the energy of activation is that for the complete reaction represented by both (i.) and (ii.) (p. 226). On the other hand the value for alcohol is calculated from k' of equation (1) which represents the unimolecular velocity-coefficient for the isomeric change of the complex, that is, for reaction (ii.) only.

(a) *Catalysis by Pyridine.*—The constant k'' of equation (3) is the bimolecular velocity-coefficient for the isomeric change catalysed by pyridine, and is therefore identical with the constant k of Lewis's equation. The values of the effective molecular diameters, that is, the mean diameters of the reactive groups of the molecules, have been taken as 4×10^{-8} cm. Since it is possible to obtain the order of magnitude only of the velocity-coefficient, it is assumed that the volume-correction introduced by Norrish and Smith is balanced by the shielding of the reactive groups of the solute and catalyst by the inert parts of their own molecules. The values of u_1 and u_2 have been deduced in the usual way from the kinetic theory. In this way the bimolecular velocity constant is calculated to be 0·084 for pyridine at 25°, compared with the experimental value of 0·227. The ratio of the observed to the calculated constant is 2·8.

(b) *Catalysis by Alcohol.*—The constant k' obtained for alcohol represents the velocity-coefficient for the isomeric change of the catalyst complex. This change may be supposed to be brought about by the acquisition of energy, by means of collision between molecules of the complex and the solvent, which may therefore be regarded as a reactant for the purpose of calculating the required constant. The bimolecular velocity-coefficient is then obtained by dividing k' by the solvent concentration. Hence, using the same values for the molecular diameters as before, the velocity constant is calculated to be 0·0072 for alcohol at 25°, and the experimental value is 0·0180, giving a ratio of observed to calculated of 2·5.

In view of the nature of the calculation, the factors 2·8 and 2·5 represent a reasonable agreement between theory and experiment, in striking contrast to the results previously obtained in solution. The reason for this difference must be sought in the nature of the reaction. It is clear that the mutarotation of beryllium benzoylcamphor, in which the activation consists merely of the opening of one, or two, rings, which are subsequently closed again in either of

two alternative positions, is a reaction of a much simpler type than the combination of trimethylamine and nitrobenzyl chloride, and similar reactions, in which a considerable rearrangement of the constituent atoms is involved.

Variation of the Velocity-Coefficient with the Solvent.

On the basis of this mechanism for the mutarotation of the complex it is easy to calculate the relative efficiencies of chloroform and carbon tetrachloride as promoters of isomeric change in presence of a catalyst. For, if the energy of activation of the complex is unaltered by the change of solvent, the relative value of k' will depend only on (i.) the diameters and (ii.) the velocities of the molecules, and (iii.) the molecular concentrations, of the solvents. If the ratio of the molecular diameters of carbon tetrachloride and chloroform is equated to the ratio of the cube roots of their parachors, the first factor will result in a diminution in the ratio 0·94 to 1 on passing from the former to the latter, the second factor produces an increase in the ratio 1·10 to 1, and the ratio of the molecular concentrations produces an increase in the ratio 1·20 to 1. The product of these three factors is 1·24, and this has been used to deduce values for the velocity-coefficients of mutarotation in chloroform when catalysed by alcohol or *p*-cresol (p. 231).

XVIII. *Magneto-Resistance and Magneto-Caloric Effects in Iron and Heusler Alloys.* *By* H. H. Potter, *Ph.D., Lecturer in Physics, H. H. Wills Physical Laboratory, University of Bristol* *.

IN a previous paper † the writer has shown that the suggestion of Gerlach and Schneiderhan ‡ concerning direct proportionality between change of resistance in a magnetic field and the change of magnetic energy is accurately true in the case of nickel. This change of resistance in the neighbourhood of the Curie point was measured both in transverse and longitudinal magnetic fields up to 7000 gauss, and was compared with the magneto-caloric measurements of Weiss and Forrer §. The resistance

* Communicated by the Author.
† Proc. Roy. Soc. A, cxxxii. p. 560 (1931).
‡ Gerlach and Schneiderhan, *Ann. d. Physik*, 5, vi. p. 772.
§ Weiss and Forrer, *Annales de Phys.* 10, v. p. 153.

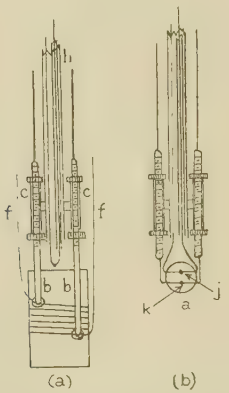
measurements have now been extended to the cases of iron and Heusler alloy, and some measurements of the magneto-caloric effect in these two substances have also been made.

Iron.

Resistance Measurements.

The resistance measurements were obtained by a voltage-current method, the specimen itself being in an evacuated tube mounted in an electric furnace between the poles of a Weiss electromagnet. The arrangements were fully described in the previous paper, so that it is necessary here to do little more than to describe a few slight modifications. In the first place, the whole apparatus had to be made of

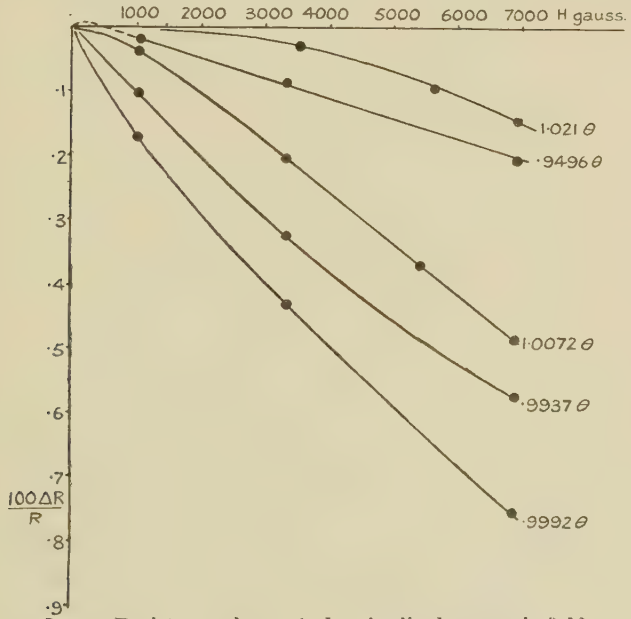
Fig. 1.



quartz instead of pyrex glass, since the Curie point of iron is about 770° C. as compared with 360° C. for nickel; secondly, to obtain greater reliability the temperatures were indicated by a calibrated platinum platinum-rhodium thermo-couple instead of copper-constantin; thirdly, the earlier method of mounting the wire for the measurements in a transverse field has been dispensed with, and the mounting previously used for the measurements in a longitudinal field has been used for both sets of measurements. The wire of which the resistance was to be measured was wound on a thin quartz sheet which was supported by two thick copper leads (*b*, *b*) fig. 1 (*a*). These leads were bent at the ends and passed through two holes in the quartz plate, to which they were secured by copper nuts threaded on to the rods. These nuts also served to secure the iron wire, which was in one piece, with the potential leads *f*, *f*. The

copper leads were secured to two quartz tubes *c*, *c*, mounted on the main supporting tube *h*. The whole was surrounded by an evacuated quartz tube of 17 mm. diameter, the tube *h* being joined to a ground-joint which enabled the quartz plate to be turned so as to be either parallel or perpendicular to the magnetic field. It is impossible with this arrangement to have the whole of the wire either parallel or perpendicular to the field, the finite thickness of the quartz plate obviously preventing this. It will be shown, however, that the transverse and longitudinal effects are identical

Fig. 2.



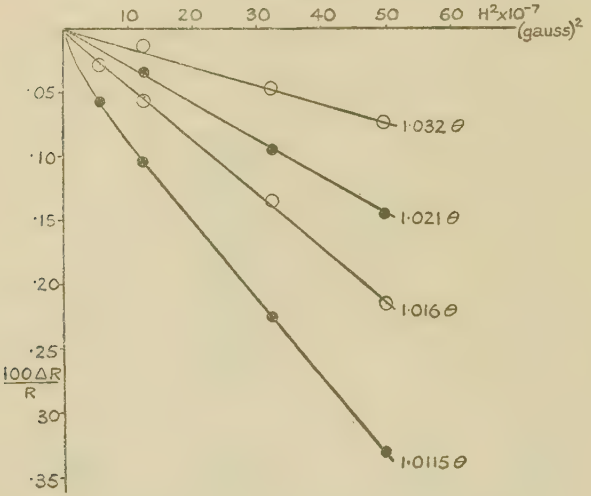
Iron. Resistance change in longitudinal magnetic field.

near the Curie point—to which region these results are confined—so that no error arises from this cause. The iron wire used was No. 36, S.W.G.

The relations between resistance change and applied field for the wire parallel to the lines of force are shown in fig. 2. The temperatures marked on the curves are given in terms of the Curie temperature (θ), which was 1050° K. The shapes of these curves correspond extraordinarily well with the shapes of the curves for nickel at corresponding temperatures. Near the Curie point $\frac{\Delta R}{R}$ is seen to change

less rapidly than the first power of H, but with rising temperature the curves change gradually in shape, until well above the Curie point $\frac{\Delta R}{R}$ varies as H^2. The significance of this will be indicated later in the paper. The curves in fig. 2 are all for the case of the wire parallel to the field. It was very difficult to get corresponding curves for the transverse effect, owing to the uncertainty in calculating the demagnetizing fields. In fig. 3, which is for temperatures above the Curie point, and for which therefore the demagnetizing field was much smaller, two curves for the

Fig. 3.



Iron. Resistance change in a magnetic field.
⊙ Transverse effect.
● Longitudinal effect.

transverse effect are included. In this figure $\frac{\Delta R}{R}$ is plotted against H^2, the straight line relations showing that in the quasi-paramagnetic condition $\frac{\Delta R}{R}$ is proportional to H^2 or to the change in magnetic energy $\frac{1}{2}\chi H^2$ (χ = susceptibility). The curve for the lowest temperature, $1{\cdot}0115\,\theta$, is not quite a straight line, showing that true paramagnetism has not been attained at this temperature.

Magneto-Caloric Effect in Iron.

The magneto-caloric effect is of course a direct measure of the change of magnetic energy which accompanies the application of an external field. The modifications in the apparatus required for its measurement are very slight indeed, and are shown in fig. 1 (*b*). The quartz plate of fig. 1 (*a*) was dispensed with, and its place was taken by a mass of pure iron *a* (fig. 1 (*b*)).

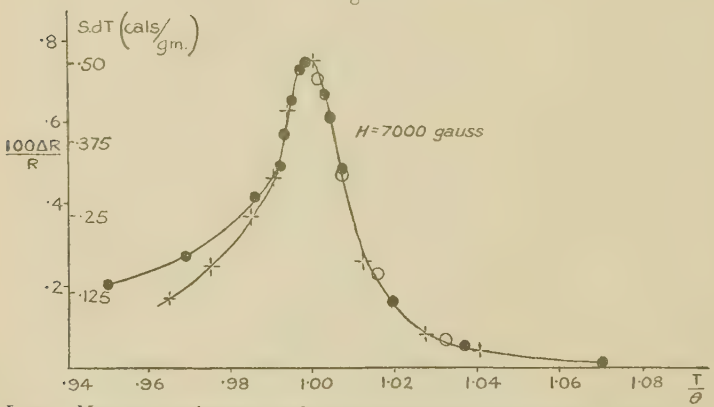
In order to examine the magneto-caloric effect two temperature measurements are necessary: (1) the temperature of the specimen, and (2) the change of temperature accompanying a given change in the value of the external field. The former was given by a platinum platinum-rhodium thermo-couple with one junction at *j* (fig. 1 (*b*)). The second junction of the thermo-couple was exterior to the apparatus and was kept at a steady temperature by immersion in water. The temperature change on magnetization was measured by a second thermo-couple of copper-constantin having one junction *k* inside the mass of iron, and the second junction only about 1·2 cm. distant but outside the iron. The latter junction was made by brazing the constantin element on to one of the copper leads *b* (fig. 1 (*a*)), the copper element being brazed on to the other lead. This thermo-couple gave practically zero e.m.f. except when the temperature of the iron was suddenly changed by a change of its magnetization. It was connected directly to a galvanometer, the deflexion on switching on the field being a direct measure of the magneto-caloric rise of temperature.

The iron specimen was an ellipsoid of revolution, with the long axis (shown perpendicular to the plane of the diagram) about twice the short axis. The long axis was parallel to the field, and consequently the demagnetizing factor was less than it would have been for a sphere, so that the effective field could be determined with greater accuracy. The thermo-junctions—although for clearness shown in the diagram placed along a short axis of the ellipsoid—were actually close together on the long axis. Contact between the iron and the junctions was obtained by jamming the thermo-junctions into tapered holes in the iron.

In fig. 4 the magneto-caloric effect for a field of 7000 gauss is shown (by the crosses) as a function of the temperature. The quantity plotted is not the rise of temperature (dT), but this rise multiplied by the specific heat (s). Obviously it is this product which represents the energy liberated, and since the specific heat changes very

rapidly in the neighbourhood of the Curie point the product $s \,.\, d\mathrm{T}$ varies somewhat differently with temperature from the variation of $d\mathrm{T}$ alone. The values of the specific heat were taken from a paper by Klinkhardt*. On the same figure are plotted the values of $\frac{\Delta R}{R}$ both for the longitudinal effect (dots) and the transverse effect (circles), the two curves being adjusted to the same height at their peaks. The transverse effect cannot be determined very accurately on account of the large value of the demagnetizing factor—2π for a long wire magnetized perpendicular to its length—combined with the fact that we have no accurate data concerning the intensity of magnetization in iron as a function of applied field and temperature. Consequently

Fig. 4.



Iron. Magneto-resistance and magneto-caloric effects as a function of temperature.

● Resistance change in longitudinal field.
⊙ Resistance change in transverse field.
\+ Magneto-caloric effect.

no values of the transverse effect are included for temperatures below the Curie point, where the demagnetizing field will be large. Even above the Curie point the demagnetizing field is appreciable, and for the points given it has been calculated using Tyler's extension of Weiss's theory †. The largest correction applied (for the point at $1{\cdot}0015\,\theta$) amounted to about 20 per cent., so that the accuracy with which the point fits on to the curve would seem to justify in some measure Tyler's extension of the ordinary theory.

* Klinkhardt, *Ann. d. Physik*, 4, lxxxiv. p. 191.
† Tyler, Phil. Mag. 7, ix. p. 1026.

Although the agreement between the resistance and magneto-caloric effects is not very satisfactory below ·99 θ, the agreement over the rest of the curve is remarkably good, and may be taken as further evidence of the close relation between $\frac{\Delta R}{R}$ and the change in magnetic energy (ΔE). The proportionality factor $\frac{\Delta E}{\Delta R/R}$ is, however, vastly different in iron and nickel, for which curves are given in fig. 8. In iron the maximum resistance change was only ·75 per cent. and the magneto-caloric heat evolution amounted to about ·50 cal./gm. In nickel the maximum resistance change was about 1·03 per cent., but the magneto-caloric effect amounted according to the results of Weiss and Forrer to only 0·1 cal./gm. These figures all refer to a field of 7000 gauss.

Heusler Alloy.

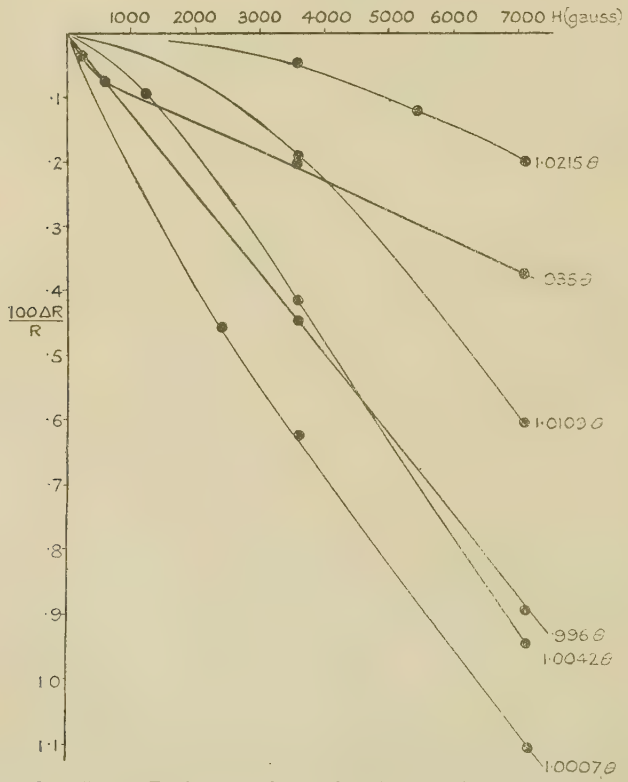
The Heusler alloy specimen used was a strongly magnetic one from a well mixed melt of constitution very near to Cu_2MnAl. The melt was cast into a narrow rod, which was annealed for 120 hours at 250° C., and then for 24 hours at 300° C. The initial long annealing at 250° C. helped to develop the strong magnetic properties, whilst the shorter annealing at 300° C. was carried out to stabilize the magnetic condition and to prevent any quick changes in properties when measurements were subsequently made at the Curie point (275° C.). A portion of the rod was ground down to about 1·5 mm. diameter, and was then further reduced in dilute nitric acid until the diameter was about 0·5 mm. This process of reducing the thickness of the specimen was carried out in two stages, since the brittleness of the alloy made reduction below 1·5 mm. on the grinding wheel somewhat hazardous. The rod was then mounted on the same apparatus as that used for the iron wire (fig. 1 (*a*)), except that the quartz plate was dispensed with, and the rod of alloy joined straight across between the two copper rods, *b*, *b*. Excellent contact at the junctions was obtained by electrolytic deposition of copper, the potential leads, which were also of copper, being joined in the same manner. With this arrangement the rod could be placed either parallel or perpendicular to the lines of force by merely rotating the ground-joint.

Resistance Measurements.

Unlike iron and nickel Heusler alloys show a decrease of resistance at room-temperatures in both transverse and

longitudinal fields. (Iron and nickel both show an increase in longitudinal and a decrease in transverse fields.) The decrease, which, when allowance is made for end demagnetizing effects, is found to be rapid for small values of the field and less rapid subsequently, amounts for both longitudinal and transverse effects to about 0 6 per cent. in a field of 7000 gauss. This effect decreases rapidly with rise of temperature,

Fig. 5.



Heusler alloy. Resistance change in a longitudinal magnetic field.

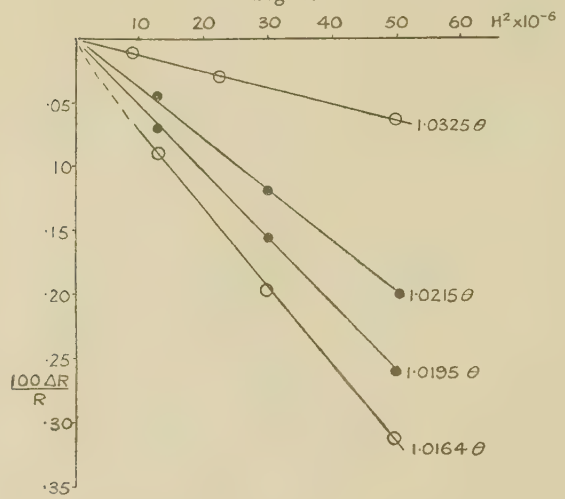
and near the Curie point gives place to effects similar to those obtained with nickel and iron. The results for longitudinal fields are shown in fig. 5, and are in good qualitative agreement with the results for iron and nickel. One slight difference, however, may be mentioned. The curve at $\cdot 935\,\theta$ (fig. 5) shows a sharp initial fall of resistance followed by a less rapid linear change of resistance with the field. The curve for iron at a corresponding temperature would show an

initial increase of resistance. This is, of course, due merely to the difference in the sign of the low temperature longitudinal effects, which have not quite disappeared at the temperature considered. If we assume that this low temperature effect has become constant where the curve is straight, then the true resistance change may be deduced from the slope of the straight part of the curve. The number of points on these curves is not as great as one would wish. The heat generated in the specimen by the magneto-caloric effect was not dissipated so rapidly as in the thin wires used in the measurements on iron and nickel. It was therefore necessary to wait some 3 or 4 minutes after every change of field before the temperature of the specimen again became steady and the resistance settled to its correct value. Owing to the difficulty of keeping the furnace temperature quite steady it was therefore necessary to cut down the number of points on a given curve to a minimum.

In fig. 6, which is for temperatures above the Curie point, and in which $\frac{\Delta R}{R}$ is plotted against H^2, two curves for the transverse effect are included. Once again it is difficult to correct the results obtained for the transverse effect for demagnetizing field. In iron the difficulty arose from our lack of knowledge of the intensity, in Heusler it arises from a different cause. It has been mentioned that owing to the brittleness of the alloy the rod was reduced in diameter by solution in nitric acid. Unfortunately the acid did not attack the rod uniformly, and the finished specimen was by no means circular in section. This irregularity made an accurate estimate of the demagnetizing factor impossible. The points for the transverse effect, which are included in figs. 6 and 7, were corrected, using a demagnetizing factor of 2π. The values of the intensity required for this correction were obtained by actual measurement on the rod before dissolving it down to the narrow diameter required for the resistance measurements. The correction amounts to about 15 per cent. at the Curie point, and of course falls off rapidly above this temperature, so that errors in estimating the demagnetizing field will not be serious for temperatures above the Curie point. This correction is somewhat greater than would be expected by comparison with iron and nickel, but is explained by the fact that the specimen used had surprisingly large susceptibility near the Curie point.

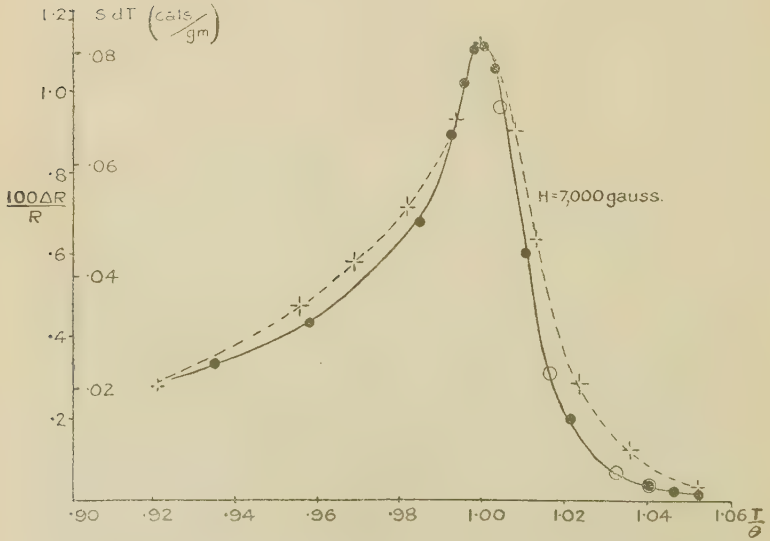
The maximum resistance change in Heusler alloy is seen to be greater than the maximum changes in either nickel or iron.

Fig. 6.



Heusler alloy. Resistance change in a magnetic field.
⊙ Transverse effect.
● Longitudinal effect.

Fig. 7.



Heusler alloy. Magneto-resistance and magneto-caloric effects as a function of temperature.
● Resistance change in a longitudinal field.
⊙ Resistance change in a transverse field.
+ Magnetic-caloric effect.

Magneto-Caloric Effect in Heusler Alloy.

The magneto-caloric effect in Heusler alloy was measured by a method identical with that used for iron. The ellipsoid used was from the same melt as the resistance specimen. It was actually the neighbouring piece from the cast rod, and was submitted to identical heat treatment. The specific heat measurements required in the calculation of the actual heat emission were taken from a paper by Sucksmith and the writer *. The specific heat curve (fig. 5 of that paper) was obtained for an alloy of the same composition as the one used in this experiment.

The magneto-resistance and magneto-caloric effects in Heusler alloy considered as a function of temperature are again strikingly similar (fig. 7). The heights of the two curves were adjusted to agree at the peaks, but the actual temperature at which the peaks occurred agreed accurately and also coincided with the temperature at which the spontaneous magnetization disappeared. The maximum value of the magneto-caloric effect appears to be less in Heusler alloy than in either nickel or iron.

Nickel.

For the sake of comparison the relation between $\frac{\Delta R}{R}$ and T, and $s.d$T and T are given for nickel in fig. 8. These results are taken from the writer's previous paper on this subject, but the temperatures are now given in terms of the Curie temperature θ, and the results are for a field of 7000 gauss and not 5000 gauss as given previously.

Discussion of Results.

The results given in figs. 2, 3, 5, and 6 show that the relation between resistance and applied field varies with the temperature. At temperatures well above the Curie point $\frac{\Delta R}{R}$ is proportional to H^2, at the Curie point $\frac{\Delta R}{R}$ varies somewhat less rapidly than H, whereas below the Curie point it is a linear function of H. Considerable evidence has been presented to show that the resistance change is proportional to the change in magnetic energy. We shall now consider how the energy varies with applied field at temperature above, at, and below the Curie point.

* Proc. Roy. Soc. A, cxii. p. 167 (1926).

Above the Curie Point.

According to the Weiss theory a ferromagnetic body when heated above the Curie temperature behaves as a paramagnetic substance. The energy can thus be written :

$$E = \tfrac{1}{2}\sigma H = \tfrac{1}{2}\chi H^2,$$

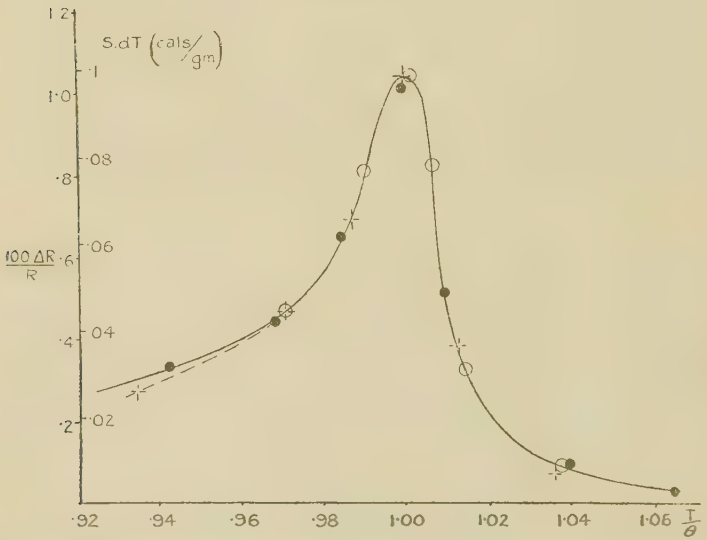
E = energy per c.c.,

σ = intensity of magnetization per c.c.,

χ = susceptibility.

$\frac{\Delta R}{R}$ should therefore be proportional to H^2 (figs. 3 and 6).

Fig. 8.



Nickel. Magneto-resistance and magneto-caloric effects as a function of temperature.

● Resistance change in longitudinal field.

⊙ Resistance change in transverse field.

\+ Magneto-caloric effect.

At the Curie Point.

The fundamental equations of the Weiss theory of ferromagnetism are

$$\sigma = \sigma_0 \tanh \alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\alpha = \frac{\mu(H + N\sigma)}{kT} = \frac{\sigma_0 m(H + N\sigma)}{\rho RT}, \quad . \quad . \quad . \quad (2)$$

μ = molecular magnetic moment,
σ_0 = intensity per unit volume at saturation,
m = molecular weight,
k = Boltzman's constant,
R = gas constant per gm. mol.,
ρ = density,
N = the constant of the intramolecular field.

At the Curie point the magnetization will be small, and so (1) can be written

$$\frac{\sigma}{\sigma_0} = \alpha - \frac{\alpha^3}{3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and in (2) T may be replaced by θ, where θ is the Curie temperature.

Using the usual equation

$$\theta = \frac{N m \sigma_0^2}{\rho R}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

from (2) and (4)

$$\alpha = \frac{\sigma}{\sigma_0} + \frac{\sigma_0 m}{\rho R \theta} H.$$

Substituting in (3)

$$\frac{\sigma}{\sigma_0} = \left(\frac{3\sigma_0 m}{\rho R \theta} H\right)^{1/3} - \frac{\sigma_0 m}{\rho R \theta} H, \quad . \quad . \quad . \quad . \quad (5)$$

$\frac{\sigma_0 m}{\rho R \theta}$ is of the order 10^{-7}, so that the second term is not appreciable unless H is large. Thus for field strengths up to several thousand gauss the intensity at the Curie point should vary as the cube root of the field.

The energy (E) is given by

$$E = \tfrac{1}{2}\sigma H_1,$$

where H_1 = total field, *i.e.*, the molecular field plus the external field ;

$$\therefore \qquad E = \tfrac{1}{2}\sigma(N\sigma + H). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Even at the Curie temperature $N\sigma$ is still very great compared with H, so that from (5) and (6)

$$E = \tfrac{1}{2} N \sigma_0^2 \left(\frac{3\sigma_0 m}{\rho R \theta}\right)^{2/3} . H^{2/3},$$

or, using (4),

$$E = \tfrac{1}{2}(9 N \sigma_0^4)^{1/3} . H^{2/3}.$$

If we put $\frac{\Delta R}{R} \propto E$, we have

$$\frac{\Delta R}{R} \propto H^{2/3}.$$

Analysis of the appropriate curves in figs. 2 and 5 gives fairly good agreement with this equation.

Below the Curie Temperature.

From equations (1), (2), and (6) we have

$$\left(\frac{\partial\sigma}{\partial H}\right)_T = \sigma_0 \operatorname{sech}^2\alpha \,.\left(\frac{\partial\alpha}{\partial H}\right)_T,$$

$$\left(\frac{\partial\alpha}{\partial H}\right)_T = \frac{\mu}{kT} + \frac{\mu N\sigma_0}{kT}\operatorname{sech}^2\alpha \,.\left(\frac{\partial\alpha}{\partial H}\right)_T,$$

$$E = \frac{\sigma_0}{2}\frac{kT}{\mu}\alpha \,.\tanh\alpha,$$

$$\left(\frac{\partial E}{\partial H}\right)_T = \frac{\sigma_0 kT}{2\mu}(\alpha\operatorname{sech}^2\alpha + \tanh\alpha)\,.\left(\frac{\partial\alpha}{\partial H}\right)_T$$

$$= \frac{\sigma_0}{2}\frac{\alpha\operatorname{sech}^2\alpha + \tanh\alpha}{1 - \frac{\mu N\sigma_0}{kT}\operatorname{sech}^2\alpha}.$$

Now provided $T << \theta$, α varies only very slowly with H, and so $\left(\frac{\partial E}{\partial H}\right)_T$ may be taken as a constant. This means a linear relation between E and H. Again, if $\frac{\Delta R}{R}$ is proportional to E this is in agreement with the experimental results.

Maximum Resistance Change and Maximum Magneto-caloric Effect.

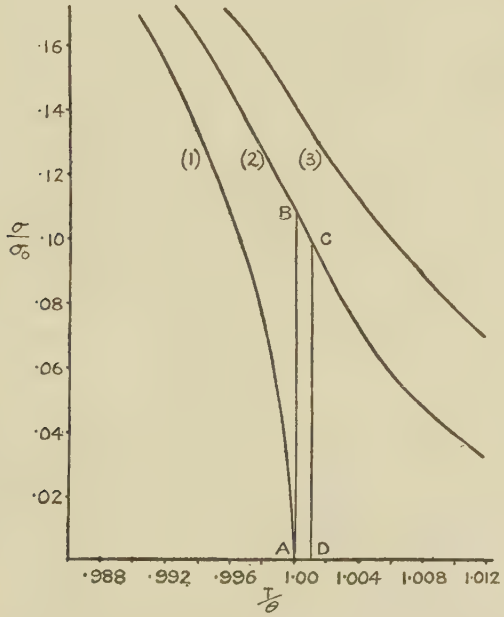
The following table shows the maximum values of $\frac{\Delta R}{R}$ and $s\,.\,dT$ for iron, nickel, and Heusler alloy for a field of 7000 gauss.

	$100\,\Delta R/R$.	$s\,.\,dT$.	$\frac{s\,.\,dT}{100\,\Delta R/R}$.
Iron	·76	.50	·66
Nickel	1·04	·10	·096
Heusler alloy	>1·12	·08	<·071

The ratios in the third column, although indicating clearly a very great difference between the three substances, are subject to certain sources of error which reduce their accuracy. In the first place $\frac{\Delta R}{R}$ is measured for an isothermal energy change,

whilst the quantity $s \cdot dT$ is necessarily measured adiabatically. The difference may be explained by reference to fig. 9. The curve (1) represents the variation of spontaneous magnetism with temperature, curves (2) and (3) are the magnetization curves of Ni and Fe respectively in fields of 7000 gauss. These are theoretical curves calculated by Tyler's method. Assume that initially a nickel specimen is in the demagnetized condition at the Curie point (A). If now it is magnetized isothermally in a field of 7000 gauss the new condition will be represented by the point B.

Fig. 9.



Theoretical magnetization curves for iron and nickel.

The energy is given by the expression $E = \frac{1}{2}\sigma(H_1 + H_2)$, where H_1 = intramolecular field and H_2 = external field. At the Curie point H_1 is still very much greater than H_2, so that $E = \frac{1}{2}N\sigma^2$, where N is the intramolecular field constant. Thus the energy change is proportional to BA^2.

If, however, the specimen is magnetized adiabatically the magnetized condition will be represented by a point C, the distance AD being proportional to the magneto-caloric rise of temperature. The energy change will be proportional to CD^2. Calculated from these curves, and using the experi-

mental value AD, the ratio $\frac{BA^2}{CD^2} = 1{\cdot}20$, or the isothermal energy change is 20 per cent. greater than the adiabatic change. An estimate can also be made from the magnetization curves of Weiss and Forrer, in which case the difference between the two effects amounts to about 16 per cent. It does not, however, change very rapidly with temperature, so that the shape of the ($s \,.\, d$T, T) curve is little affected. The ratio, calculated in the same way for iron and Heusler alloy, is very near the value for nickel, so that the only effect it has on the results of this paper is to reduce all the values of $s \,.\, d$T in the same proportion.

Secondly, in the case of Heusler alloy there is an error in the resistance measurements. The temperature changes due to the magneto-caloric effect always introduce a change of resistance opposite in direction to the magneto-resistance change. Even though a certain time was allowed for dissipation of the heat generated on applying an external field the measured ΔR was certainly slightly less than the value for an isothermal change of the field. This error is appreciable only in the case of the alloy, which was in rod form. In the cases of iron and nickel the specimens were fine wires of such low heat capacity that the heat generated by the magneto-caloric effect was lost by radiation in a few seconds.

With only three values of $\frac{s \,.\, d\mathrm{T}}{\Delta \mathrm{R}/\mathrm{R}}$ one hestitates to make suggestions as to the cause of its variation for the three substances. It is significant that the ratio increases with increasing Curie temperature. The relation is possibly of the form $s \,.\, d\mathrm{T} = \mathrm{A}\theta^n \Delta \mathrm{R}/\mathrm{R}$, where A and n are constants, n being about 3.

Summary and Conclusions.

Measurements have been made on the magneto-resistance and magneto-caloric effects in iron and Heusler alloy. Further evidence of the direct proportionality of the magneto-resistance change to the change in magnetic energy has been obtained, but it has been shown that the proportionality factor varies considerably for different substances.

My best thanks are due to the Colston Research Society of the University of Bristol for a grant towards the expenses of this investigation, and to Prof. Tyndall for his interest in the work.

XIX. *On the Variations in the Refractive Index of Benzene during Intensive Drying.* *By* J. J Manley, *M.A., D.Sc., Oxon, Fellow of Magdalen College, Oxford* *.

Introductory.

IT is well known that Prof. H. B. Baker has, by intensive drying, brought about notable changes in the boiling-point B.P. of benzene. Similar and equally interesting results have been obtained with certain other liquids, as, for example, carbon tetrachloride and hexane.

The observed variations in the B.P. lead, as I have already pointed out elsewhere †, to the almost inevitable conclusion that during drying, corresponding changes, although of a much smaller order, occur in the other physical "constants" of the liquid.

Now, if such changes can be detected and measured, we acquire additional and valuable data for elucidating the underlying cause of the growths in the B.P.

Preliminary experiments having shown that the expected variations in certain constants other than the B.P. do accompany the progressive and final dehydration of benzene, effect was given to plans made for accurate determinations of the same.

In this communication we confine ourselves chiefly to a consideration of certain variations which occur in the refractive index during the intensive drying of benzene. The changes in volume also resulting from prolonged dehydration will be dealt with in another paper. We first describe the purification of the benzene used as a standard.

Preparation of a Standard Benzene.

The benzene used as a standard in this research was of the purest obtainable. Shaken for a considerable time with concentrated sulphuric acid, the latter remained colourless; but frequent shaking for some days resulted in the production of a slight tint. After treating with sulphuric acid the benzene was washed, first with water, then with sodium hydrate solution, and finally with "conductivity" water. When it had been dried over fused and pure calcium chloride it was distilled, use being made of an apparatus previously rendered chemically clean and dry. Having

* Communicated by the Author.

† 'Nature,' cxxiii. p. 907 (1929).

rejected a first small portion *, the main distillate was collected and subsequently slowly cooled until about three-quarters of it had crystallized. The residual liquid was then drained away, the crystals liquefied, and the benzene thus repurified stored in a chemically clean and dry bottle ready for use.

The Refractive Index of Standard Benzene.

(1) *The Spectrometer and Prism.*—For measuring the refractive index μ of the standard benzene, there were available the Royal Society's spectrometer and hollow quartz prism employed in former researches †. The graduated silver circle of the spectrometer, some 27 cm. in diameter, was calibrated as described elsewhere ‡. With the aid of two attached reading-microscopes fitted with micrometers, angular values were determinable with an accuracy of 2″ of arc.

For securing the parallel-plane plates to the prism, a thick oleum of metaphosphoric acid was prepared from pure phosphorus pentoxide. The oleum was smeared along the edges of the prism, the plates applied and gently pressed, and the adhesive thus made to flow towards the centre. The flow was accelerated and completed by a "Hyvac" pump operating through the aperture made for charging the prism. Superfluous oleum having been removed, the edges of the joints were coated with Canada balsam; thus the oleum was prevented from deliquescing, and at the same time the adherence of the plates increased and rendered more permanent.

Next, the newly built prism was charged with standard benzene and the aperture closed with a glass cover-slip coated beneath with the prepared oleum. Lastly, a short glass tube was luted to the prism so that it encircled the cover-slip, and into this mercury was poured and the adhesive thus protected from moisture. The prism was then placed upon the levelling-table of the spectrometer. Subsequently its refracting angle was measured and found to be $60^\circ\ 6'\ 12''$.

Determination of the Angle of Minimum Deviation for the D line.

It will be noted that, by closing the prism as described, direct observations of the temperature of the contents were

* The first portion is almost invariably milky. Apparently traces of water unremovable by calcium chloride are, as the distillation begins, concentrated in the vapour of the boiling liquid. The milkiness disappears on warming or on filtering through dry paper.

† Proc. Roy. Soc. lxix. p. 108.

‡ *Annalen der Physik*, pp. 575–579 (1901).

rendered impossible. The difficulty thus presented was met as follows :—A bottle, oval in form and having thick walls, was fitted with a thermometer graduated to 0°·1 C. and filled with benzene; it was then tightly corked and placed against the vertical base of the charged prism. Finally, the whole was enclosed by an aluminium cylinder, through the lid of which the thermometer stem projected. The two windows cut in the cylinder for the transmission of light could be shuttered at will.

The reliability of this plan for ascertaining the temperature of the benzene in the prism had previously been tested when, with water in both prism and bottle, the readings of a standard thermometer in each were during an extended period wholly consistent. Doubtless this was due not only to the effectiveness of the protecting aluminium cylinder, which was polished without and blackened within, but was also largely dependent upon the fact that the spectrometer was set up in a room facing N.E. and having the daily small temperature variation of 2° C.

When the spectrometer had been adjusted, tentative experiments were made to discover remediable imperfections. These having been corrected, twelve independent measurements of the minimum deviation of the *D* line were made. Of these, six were carried out during the morning and the remaining six during the evening of a day for which the maximum and minimum temperatures were respectively 18° and 16° C. and the mean temperature 16°·70 C. Within these limits the variation in μ for the standard benzene was ·000610 per 1° C. Using this coefficient, the twelve independent values for μ were each and all reduced for the temperature of 16°·70 C. and the final mean calculated. It was thus found that

$$\mu_{16\cdot7_{[D]}} = 1\cdot50377_1 \pm \cdot000007.$$

The variation of $\pm$·000007 corresponds to an error in temperature of $\mp$0°·01 C.

In all that follows $1\cdot50377_1$ was used as the standard value for μ. A brief description may now be given of the plan adopted for measuring differentially the successive increments in μ during intensive drying.

Apparatus used for the Determination of the Variations in μ during Intensive Drying.

The accuracy attainable in determining μ by the prism method is not, according to my experience, greater than that represented by five units in the sixth place of decimals ; and

as this degree was in the present instance wholly insufficient, use was made of a Jamin interferometer. The instrument, built by Messrs. A. Hilger, had glass containing tubes 25 cm. long; and owing to the inadmissibility of cements in general, the parallel-plane glass windows were of the adhesed or fused-on type. One great advantage of such tubes is that they can be safely cleaned by the most efficient methods.

As a result of some preliminary measurements it was deemed necessary for the purpose in hand to modify and elaborate the interferometer. The following changes were therefore made :—

(*a*) The beam of light passing to the interferometer was greatly reduced. This was done by substituting for the makers' aperture, some 18×12 mm. in diameter, one that was circular and 1 mm. only in diameter. This aperture was cut in a bright aluminium plate.

(*b*) A 25-watt lamp used with the instrument was surrounded by a screen, and a horizontal tube projecting from this was directed towards the interferometer. The tube was fitted with a diaphragm. Also a clear glass cylinder, filled with water, was suitably placed in front of the 1 mm. aperture. Possible heating effects were thus reduced to a minimum and the lamp-light concentrated.

(*c*) The interferometer tubes were enclosed by an aluminium cell, the walls of which were bright without and black within. The required light entered and left the tubes and their contents through small circular windows cut in the two ends of the cell. These windows were fitted with shutters.

(*d*) A fine adjustment of the lever-type was added to the compensator. The lever, having an effective length of 6 inches, was, as usual, controlled by a screw working in opposition to a spring.

(*e*) A small reading-microscope was set up in conjunction with the divided circle and its vernier. Angular measurements were thus readable with an accuracy of 3′ of arc.

These several modifications added much to the convenience of working and ensured greater precision.

Determination of a Zero Reading for Standard Benzene.

As a necessary step in the determination of the variations in μ during the intensive drying of benzene, both interferometer tubes were first filled with standard benzene and their tubulures closed with caps lubricated with metaphosphoric acid (*vide supra*) ; the tubes were then placed *in situ* and compensator readings taken at various temperatures. Theoretically these readings should be invariable. Practically,

slight differences appear. With due care such differences are, however, insignificant and wholly negligible. The mean value of the whole series of readings was accepted as the true one for the standard benzene ; and with this as zero all other and subsequent readings were compared.

One interferometer tube (henceforth termed the comparison tube) was now emptied and dried; it was then attached to the ground and lubricated junction of the terminal glass spiral of the drying apparatus (*vide infra*). The other interferometer tube was left undisturbed and its contents used throughout as the standard of reference.

Plan adopted for the Drying and Periodic Examination of Benzene.

In his papers dealing with the changes in the B.P. of benzene Prof. Baker has, with the aid of illustrative figures, fully described the apparatus used by him for intensive drying. In this research his methods have in principle been strictly adhered to ; hence a brief description, unaccompanied by drawings of my own apparatus will here suffice. The apparatus used for a first series of experiments was as follows :--

To the mouth of a globular flask was fused a vertical condenser, near the upper end of which was a long side-tube. This side-tube sloped upwards for a short distance and then passed vertically downwards through a water-jacket, below which it finally ended in a spiral--this to ensure flexibility. To the end of the spiral was fused a cap, accurately ground to fit the inlet of the comparison tube of the interferometer. The exit was also fitted with a ground-on glass cap to which was fused a drying-tube filled with phosphorus pentoxide *. Both caps were lubricated with the prepared oleum (*vide supra*), firmly seated, and then enveloped with mercury. These operations having been completed, the flask was then charged by first introducing a quantity of phosphorus pentoxide and then the required benzene. Finally, the apparatus was closed by first softening and then drawing off the upper and open extremity of the reflux condenser. For the purpose of heating, the flask was immersed in a bath of medicinal paraffin. Experiments were made in the following way :—

First, the bath was suitably heated and the benzene gently and continuously boiled for a known period †. Next, the

* The phosphorus pentoxide used in these experiments was purified by ozonized air, as described in the J. C. S. cxxi. pp. 331–337.

† Boiling was resorted to with the object of increasing the rate of drying.

reflux condenser was rendered ineffective and the benzene vapour allowed to pass over into the side-tube, wherein it was condensed by the action of the water-jacket and delivered into the empty comparison tube.

When this was full the reflux condenser was again activated and the residual benzene boiled for a second known period. At intervals during this second period interferometer readings were taken, and from the mean value of these was calculated the first increment in μ resulting from the treatment just described. The following example will assist in making the procedure clear :—

Experiment 1.

(*a*) Both interferometer tubes filled with standard benzene.	Compensator micrometer reading.	81°·7
(*b*) Reference tube filled with standard benzene and comparison tube filled with first distillate.	Compensator micrometer reading.	89°·0
	Difference	7°·3

From a table of calibrations the difference 7°·3 was found to be the equivalent of n fringes in sodium light. Calculating the increment according to the formula

$$\mu_1 - \mu_0 = n\lambda/l,$$

in which μ_1 and μ_0 are the respective indices of the first distillate and the standard benzene, λ the wave-length of sodium light, and l the length of the interferometer tubes in cm., we have

$$\mu_1 - 1{\cdot}50377_1 = \frac{20{\cdot}2 \times 5890 \times 10^{-8}}{25} = 4759 \times 10^{-8}\ *.$$

Having thus completed the first determination the second was continued and ended as follows :—

When the time assigned for the second period of boiling had elapsed the first distillate was quickly withdrawn from the comparison tube and the protecting drying-tube instantly re-attached to its tubulure. Another portion of benzene was then distilled and the comparison tube refilled. Subsequently the residual liquid was boiled during a third period ; and

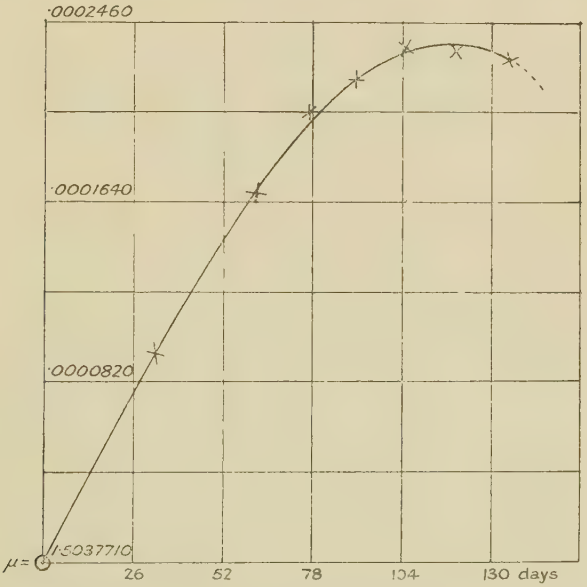
* It was found that the temperature coefficients of the refractivities μ_0 and μ_1, $\mu_2 \ldots \mu_8$, were indistinguishable. Hence the differential method here employed and used throughout was wholly admissible.

whilst this was in progress new interferometer readings were taken. With the aid of these the second increment in μ was calculated as described above. Continuing thus, eight distillates were in the course of six months collected and the corresponding increments in μ determined. The results yielded by this series of experiments are shown graphically in fig. 1.

Second Determination of the Increments in μ.

The second series of experiments was carried out with a somewhat different and smaller apparatus. The new

Fig. 1.



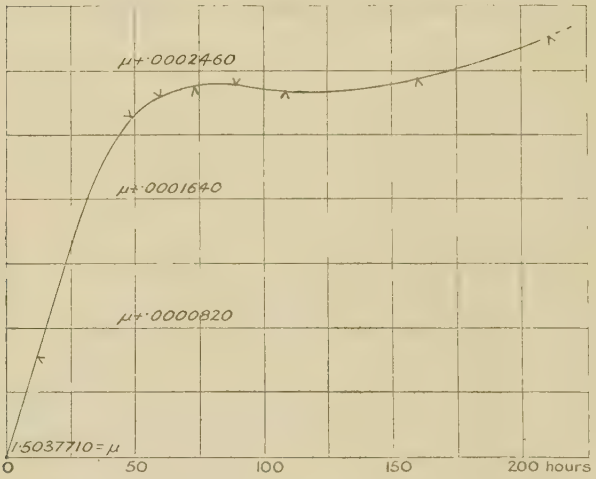
apparatus, like the other, included reflux and condensing systems. The benzene undergoing intensive drying could therefore be boiled for lengthy periods without appreciable loss, or be distilled into the comparison chamber of the interferometer. It differed, however, from the old in that the tube delivering the distillate just touched the floor of the comparison chamber and was in form capillary. Also the top of the reflux condenser, instead of being closed by fusing, was left open and fitted with a ground-in tube filled with phosphorus pentoxide. Under these circumstances the benzene which had been distilled could be re-transferred to the boiling-bulb by applying suction to the drying-tube.

The apparatus was rendered chemically clean and dry and then charged with standard benzene and phosphorus pentoxide: the drying-tube having been placed *in situ*, the second series of experiments was proceeded with and completed in accordance with the general procedure followed in the first series.

For these additional experiments the benzene was boiled for a total period of 200 hours and the distillates collected for the determination of the increments in μ at eight unequal but convenient intervals.

The results are graphically represented in fig. 2.

Fig. 2.



It may be noted that a chief advantage of the second plan lies in the fact that by its use great economy of time was effected; and that whereas in series 1, 100 days were required for the attainment by μ of a maximum value, in series 2 less than 70 hours sufficed for the same purpose. Doubtless this difference in time was partly due to the employment in the two cases of very dissimilar volumes of benzene. But it would appear that a second and contributory cause must have arisen; for in series 1 it was necessary before any one of the eight successive distillates could be withdrawn, to remove the drying-tube from the exit of the comparison chamber; and this, as Prof. Baker has clearly shown, would result in an almost immediate absorption of moisture. Thus

the time required for any given degree of intensive drying would be increased.

Next we observe that the character of the chief portion of the second graph (fig. 2) entirely conforms to that of the first (fig. 1). Hence the two are mutually confirmatory. From this we conclude that the small decline in growth which immediately follows the attainment of a maximum value by μ is to be regarded as real and not accidental.

Lastly, we have, from the terminal portion of the second graph, further evidence as to the effect produced upon μ by continued intensive drying; and it will be seen that, after the slight decline just noted, the growth was resumed and was still proceeding when the experiments ended. Other experiments are now being made with the object of determining a limiting or major value for μ; but in the light of Prof. Baker's work, the results cannot be known for some years to come. Meanwhile, those already obtained appear to merit publication without undue delay.

Dehydration of Benzene by Sodium and Potassium.

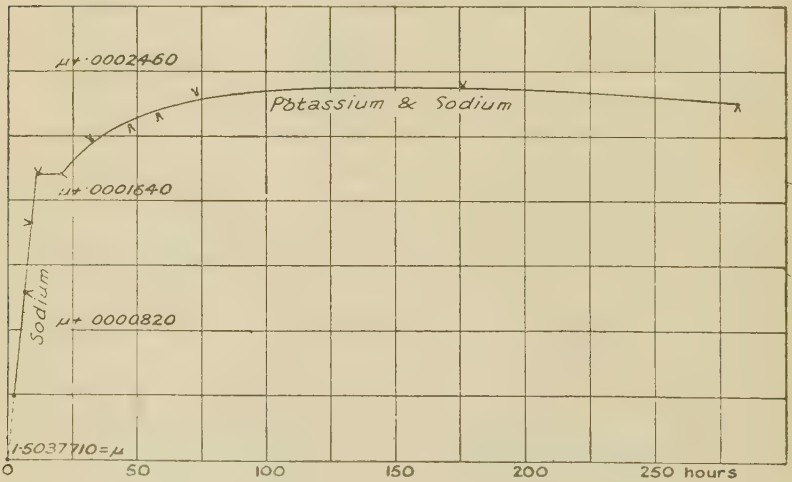
Having concluded the experiments just described an attempt was made to effect, by decomposing the retained water, a more rapid and possibly a more complete dehydration of benzene. For this purpose use was made of an apparatus precisely similar to that employed for the second series of experiments with phosphorus pentoxide. The procedure also was unchanged; and therefore the two interferometer tubes were, at the outset, again filled with standard benzene and the zero of the instrument re-determined. Next, the comparison tube attached to the condenser was emptied and the new experiments commenced at a given moment by introducing into the benzene contained in the boiling-bulb some pellets of sodium *. The sodium caused an immediate but feeble evolution of gas from the calcium chloride-dried benzene; and this persisted for some hours. The benzene was now boiled for a convenient time and then distilled into the empty interferometer chamber and the first increment in μ determined. Next, the distillate was drawn back into the bulb and boiled with the sodium

* For these experiments the pellets were prepared as follows:—First a piece of sodium was placed in benzene and its outer portions cut away. The metal was then repeatedly washed and finally covered with benzene; then it was cut into small pieces. Potassium pellets were prepared in the same way.

for a second period; and so on. Proceeding thus, μ assumed a constant value within about ten hours (fig. 3).

At this point the prepared potassium pellets were introduced, with the result that the evolution of hydrogen was renewed. Boiling was then resumed and the periodical measurements continued. During this additional treatment μ slowly increased and acquired a second maximum value within 140 hours. Lastly, the benzene was boiled with the sodium and potassium pellets (some of which had now formed a bright alloy), for a further period of 130 hours. In this way μ was slightly reduced. The observed reduction is,

Fig. 3.



however, consonant with the results obtained with phosphorus pentoxide in series 1 and 2. In fig. 3 the successive increments are as before, plotted against the corresponding intervals of time. On comparing the resultant graph with those of figs. 1 and 2, we see that the dehydrating powers of sodium and potassium are inferior to that of phosphorus pentoxide, and that the hoped for superiority was not realized.

An experiment may now be described in which μ was gradually increased by the action of phosphorus pentoxide not in contact with the benzene. The experiment, the simplest possible, was as follows :—

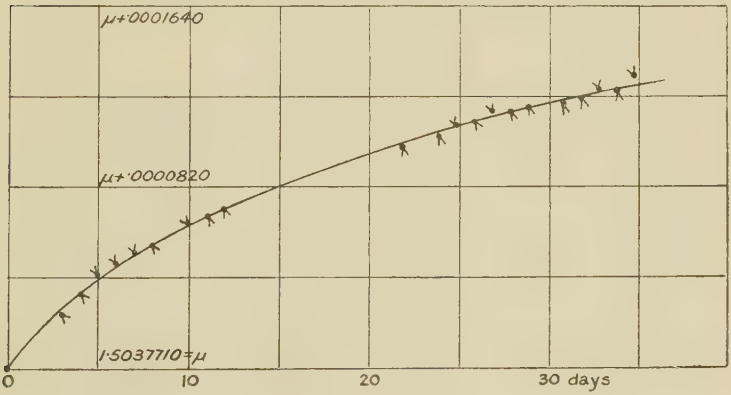
Changes observed in μ during the Drying of Benzene Vapour.

To begin with, both interferometer chambers were charged with standard benzene, a series of compensator readings taken, and from these a mean value, regarded as zero, calculated.

Next, two drying-tubes, each filled with phosphorus pentoxide, were attached, the one to the inlet and the other to the outlet of the second interferometer chamber.

Lastly, compensator readings were again taken, now periodically, for the space of a month, the successive increments in μ determined, and the data thus obtained set out graphically (fig. 4),

Fig. 4.



In this experiment dehydration, as revealed by the continuously changing value in μ, must have been due to the passing of benzene vapour to and from the drying reagent and so back into the liquid. Under the circumstances it is perhaps surprising that μ was so markedly affected and that the growth was not irregular in form.

The next experiment to be dealt with is probably the most suggestive and informative of all.

Of the Temporary Value of μ following the Liquefaction of crystallized and partly dried Benzene.

The experiments now to be described were carried out with standard benzene made wet by shaking with "conduc-

tivity" water. Both interferometer tubes were filled with the wet liquid, placed *in situ*, and then used as follows:—

Firstly, a series of observations was taken and the zero of the instrument calculated.

Secondly, at a pre-determined moment, phosphorus pentoxide was introduced into the experimental tube, the contents shaken, and a new series of observations commenced, readings being taken at short intervals for about ten hours. These were followed by others taken daily. At the end of a week the daily growth in μ had become, for the purpose in hand, a negligible quantity.

Thirdly, it being winter, the room in which the experiments were being conducted was for a period left unheated. Consequently the temperature fell to about 2° C.; and as a result the partly-dried benzene became almost wholly crystalline, whilst the wet benzene remained entirely liquid. Attempts made to induce crystallization in the wet benzene ended in failure.

Fourthly, the experimental tube containing the crystallized benzene, was removed from the interferometer, momentarily immersed in water at 10° C., and then for a time tilted up and down, These last two operations were continuously alternated until no crystals remained. Liquefaction was thus effected at a temperature differing but slightly from the melting-point.

Finally, the experimental tube containing the liquefied benzene was replaced in the interferometer and observations again taken at short intervals until further changes in μ were insignificant. The results thus obtained are depicted in fig. 5.

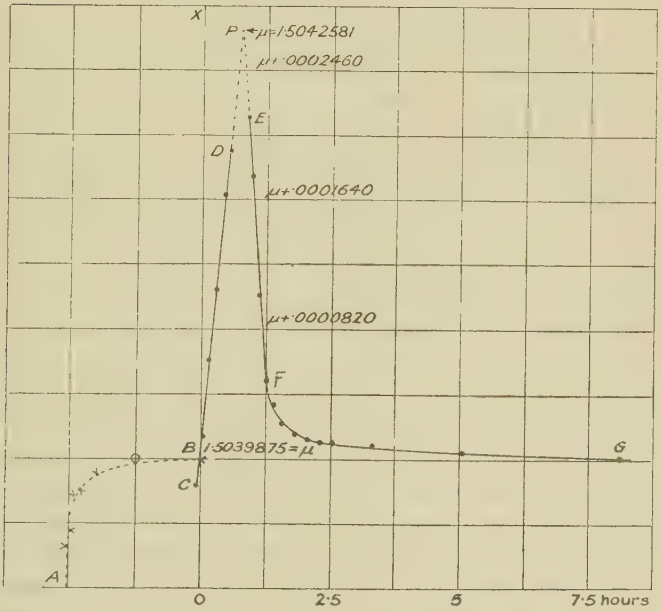
In order that the legitimate conclusions, to which this graph rightly understood, leads, a few remarks may be ventured as to the conditions governing the behaviour of the benzene.

First, we observe that although care was taken to liquefy the crystals at the lowest temperature possible, there must inevitably have been some fleeting upward movements in the temperature of the liquid; and this upward trend would be the greatest and most prolonged just at the time the last vestige of the crystalline mass became liquid. Up to that moment any slight rise in temperature would be quickly and automatically corrected by the melting benzene. Hence a determination of μ following *instantly* upon complete liquefaction, would, if measured as before in terms of the standard benzene, reveal a distinct *lessening* in value. Such a temporary depression is actually shown by the portion BC

of our graph. That this view is true will be readily granted when it is remembered that a variation of 1° C. corresponds to a change in μ of ·00066. The depression BC is equivalent to a temperature in excess of that of the standard benzene, approximating 0°·03 C. (The whole limb, CP, corresponds to about 0°·43 C.)

Secondly, viewing the graph as a whole, and for the moment neglecting the effect of temperature, we conclude that, on slowly melting dried and crystallized benzene, some

Fig. 5.



fraction of the resultant liquid consists of molecular assemblages of unusual complexity and density. Further, from the limb EG of the graph, we conclude that such assemblages, when produced as here, within *partially* dried benzene, are, owing to the disintegrating influence of residual water, more or less quickly resolved into others less dense but stable. We have no evidence of the existence of the more closely packed assemblages within wet benzene; but that before us seems clearly to indicate that as dehydration proceeds the denser assemblages are continuously formed, and that in number a maximum and permanent value is reached

with the withdrawal of the last trace of water. It will therefore be seen that if this interpretation of the results obtained interferometrically be true, then the cause of the rise in the B.P. resulting from an intensive drying of benzene is at once apparent.

Discussion of the Results.

We now take a brief review of the whole graph (fig. 5). The depression BC has already been sufficiently dealt with, and from what has been said as to the cause of the depression it will be evident that the ascending value of μ, as represented by BD, is due to a final readjustment of the temperature of the liquid benzene, following the introduction of the tube into the interferometer. The limb EFG is quite obviously representative of the rate of disintegration of the exceptionally massive assemblages already referred to. Also it will be seen that within the eight hours immediately following the complete liquefaction of the partially dried and crystallized benzene and whilst the temperature of the laboratory remained at 5° C., the whole of these assemblages, as shown by the decrease in the value of μ, had reverted to normal ones. Extrapolating both limbs of the graph, intersection occurs at P: whence a major value for μ is determinable and found to be 1·5042581, and this shows a maximum temporary increase of ·0002706. Left thus, our review would be incomplete, for upon reflection it would appear that, in respect of the more massive molecular assemblages, disintegration sets in immediately after the liquefaction of the solid benzene. Owing, however, to the initial small changes in the temperature already mentioned, the effect is not at once apparent. We approach more nearly to the true temporary value of μ by extrapolating FE in the direction of P until the curve intersects the axis OX. Doing this, we then find the increment in μ ·0006052; and this value is 2·23 times greater than that corresponding to the apex P. But even this new and larger increment is probably too small, for in a curve of the type shown in fig. 5 the first or upper portion is more steeply inclined than is the limb FE. Whence it follows that the altitude attained by extrapolating FE is less than the characteristic one. Consequently the true increment is greater than ·0006052, and the number of the transient and more optically dense molecules of benzene larger than a cursory glance at the graph (fig. 5) might lead one to expect. For a fuller and more critical investigation a new interferometer has been designed and built. In due course we

therefore hope to publish the results of some additional experiments which have been projected. A few brief remarks may now be made upon some observed variations in the B.P.

Variation in the B.P. during Intensive Drying.

During the progress of the several experiments with phosphorus pentoxide, and also with sodium and potassium, periodic measurements of the B.P. of the benzene were carried out and reduced for N.P.

In the case of phosphorus pentoxide there were seventeen determinations. The maximum value observed was 81°·35.

Whilst experimenting with sodium and potassium nineteen determinations of the B.P. were made. The highest value was 82°·02, the lowest 81°·28, and the mean of the whole 81°·56 C.

In both series of experiments the changes in the B.P. were chiefly irregular ; hence the impossibility of correlating them with time-intervals.

Upon one occasion only was there any well-marked *increase* in the B.P. This was observed whilst distilling benzene in the presence of sodium. The distillation commenced and continued for some time at a normal rate, whilst the liquid was to all appearance perfectly quiescent and the B.P. quite steady at 84° C. Finally, however, the benzene boiled up suddenly and the temperature fell to 82°·3 C. The pressure at the time happened to be almost exactly normal.

The above-named facts illustrate the erratic nature of B.P. determinations made during the *earlier* stages of intensive drying. They also assist in accounting for the divergences of the conclusions reached by researchers who have attempted a repetition of the original investigation. We conclude with a word upon the relative effectiveness of certain drying reagents.

Note upon the relative Dehydrating Effects of certain Reagents.

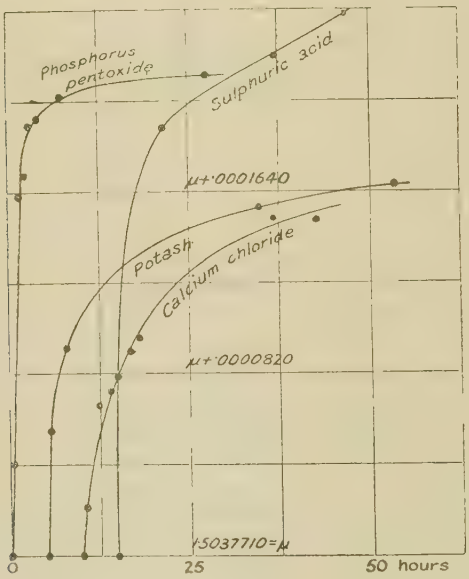
In connexion with this research it seemed desirable to compare the dehydrating effects of granular calcium chloride, and also of newly re-fused potash, with those of our pure phosphorus pentoxide. Accordingly the following experiments were made :—

Firstly, both interferometer tubes were filled with pure, but in this case damp, benzene, and the zero of the instrument determined.

Secondly, at a known moment, one of the drying reagents was dropped into the experimental tube of the interferometer and the contents agitated. Later, the increment in μ was measured and the time noted. Then the tube was again shaken and the growth in μ re-measured. Proceeding thus, experiments were continued until further changes were negligible.

Thirdly, the experimental tube was emptied, washed, and dried ; then it was re-charged, and the effect upon μ of a

Fig. 6.



second dehydrating reagent determined. The results of the several tests are graphically shown in fig. 6. It will be seen that as a drying reagent calcium chloride is inferior to potash. The effects produced by sulphuric acid are interesting ; and at first it might appear that the dehydrating power of the acid is fully equal if not superior to that of phosphorus pentoxide. The true drying effect, is, however, in some degree masked by the formation and consequent presence of benzenesulphonic acid, a minute quantity of which would augment the value of μ.

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XX. *The Magneto-Optical Dispersion of Organic Liquids in the Ultra-violet Region of the Spectrum.*—Part IV. *The Magneto-Optical Dispersion of Acetic Anhydride, Normal Butyric Acid, and Normal Ethyl Butyrate.* *By* W. J. Lewis, *B.Sc.*, *and* Prof. E. J. Evans, *D.Sc.*, *Physics Department, University College of Swansea* *.

THE apparatus and experimental methods employed in these investigations have been described in detail in Part I. †, and consequently only a brief reference to these points is necessary.

The light from a tungsten arc falls on a Bellingham-Stanley polarizing unit designed for work in the ultra-violet, and then traverses the liquid contained in a quartz polarimeter tube, which is placed symmetrically inside the core of a solenoid. The polarized beam, after emerging from the liquid, passes through the analyser and a quartz fluorite lens, which brings it to a focus on the slit of a quartz spectrograph. As the beam of light emerging from the polarizer consists of two semicircular fields with a horizontal line of demarcation, the vibrations in one of the fields being polarized at a slight angle with those in the other, two spectra (one immediately above the other) are obtained at the camera end of the quartz spectrograph.

The analyser is set at zero by adjusting its position so that these two spectra have the same intensity throughout their length when the magnetic field of the solenoid is not excited. There are four positions of the analyser for which this is possible ; but one of the two positions of minimum intensity is chosen, as the polarimeter is then in its most sensitive position. The analyser is then rotated through an angle θ, and a photograph taken with the magnetic field excited. A second photograph was also taken on the same plate, corresponding to a rotation θ on the opposite side of the zero with the magnetic field reversed. An examination of the photograph plate shows that there is a line of definite wave-length, which has the same intensity in the upper and lower half of each spectrum. Let λ be the mean wave-length of this line, as determined from the photograph, and θ_1 the rotation at this wave-length due to the quartz ends of the polarimeter tube : then the value of Verdet's

* Communicated by the Authors.

† Stephens and Evans, Phil. Mag. x. p. 759 (1930).

constant δ of the liquid for wave-length λ is given by the equation

$$\theta_2 = \theta - \theta_1 = \delta \Sigma H l,$$

where the summation is taken over the length of the liquid column. The current passing through the solenoid was kept constant at two amperes, and the magnetic field H at different points along the axis of the solenoid had been accurately measured. The value of $\Sigma H l$ was 12270 cm. gauss.

The refractive indices of the three liquids in the visible region of the spectrum were determined by means of an accurate spectrometer in the usual manner, and in the ultra-violet region of the spectrum photographically by means of the quartz spectrograph in which the Cornu prism had been replaced by a hollow glass prism closed by plates of optically worked fused quartz.

The results obtained by the two methods overlapped over a region of the visible spectrum. The mode of procedure in the photographic determinations was as follows :—

Three slightly overlapping copper spectra were photographed with the hollow prism filled with (*a*) the standard liquid, (*b*) the liquid under investigation, and (*c*) the standard liquid. The standard liquid employed was normal butyl alcohol, whose refractive indices in the visible and ultra-violet regions of the spectrum had been determined by Stephens and Evans *. The refractive index of the liquid under investigation for a wave-length λ_2 can be determined by identifying, in the spectrum produced by the standard liquid, a line of wave-length λ_1, which coincides in position with the line of wave-length λ_2 in the spectrum of the liquid under investigation. Then the refractive index of the liquid for a wave-length λ_2 equals the refractive index of the stardard liquid for the wave-length λ_1. The temperatures of the liquids were determined immediately after each exposure by means of a small calibrated mercury thermometer, and the slight shifts in the positions of the spectra were due to small temperature changes. The values of the temperature coefficients of refractive index of each liquid were found by taking photographs of two slightly overlapping copper spectra by means of the hollow prism containing the particular liquid at two known temperatures. From the resulting displacements in the positions of the

* *Loc. cit.*

spectrum lines the temperature coefficients corresponding to different regions of the spectrum could be determined. From a knowledge of the temperature coefficients the refractive indices of the liquids at temperatures differing by a few degrees from those at which they were determined could be calculated.

The liquids employed in this investigation were obtained from Dr. Schuchardt, of Görlitz, and each was subjected to a process of fractional distillation before determinations were made of the refractive indices and the magneto-optical rotations.

The experimental results have been examined in relation to Larmor's * theory of magneto-optical rotation. According to this theory Verdet's constant δ is given by the expression

$$\delta = \frac{e}{2mC^2} \cdot \lambda \cdot \frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the refractive index, $\frac{e}{m}$ is the ratio of the charge to the mass of the resonators, and C the velocity of light. In the above expression the charge e is measured in electrostatic units and the magnetic field in electromagnetic units.

If the magneto-optical dispersion of each of the liquids in the region of the spectrum investigated is controlled by one absorption band in the ultra-violet, and the natural dispersion by an equation of the Ketteler-Helmholtz type, it can be shown that

$$\phi = n\delta\lambda^2 = \mathrm{K}\left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2}\right)^2, \quad . \quad . \quad . \quad . \quad (2)$$

where K is a constant and λ_1 the wave-length of the absorption band in the ultra-violet.

In addition, it can be shown by combining equations (1) and (2) and the natural dispersion equation

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

that the value of $\frac{e}{m}$ is given by $-\frac{2\mathrm{K}C^2}{b_1}$.

* Larmor, 'Æther and Matter,' Appendix F.

Experimental Results.

Natural Dispersion.

Table I. (*a*).

Visual Determinations.

Wave-length in microns.	Refractive indices. Acetic anhydride at 16° C.	Ethyl butyrate at 13° C.	Butyric acid at 13° C.
·6678	1·3897	$1·3936_6$	1·3988
·5876	1·3920	$1·3958_2$	1·4011
·5016	1·3959	1·3996	1·4051
·4922	1·3966	$1·4002_6$	1·4057
·4713	1·3978	1·4015	1·4070
·4472	$1·3995_5$	$1·4032_5$	1·4086

Table I. (*b*).

Photographic Determinations.

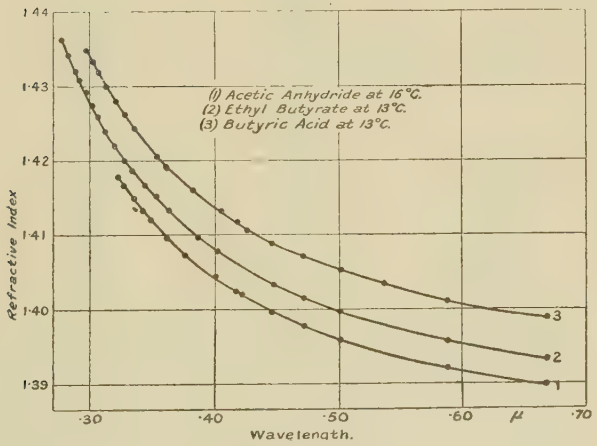
Normal Butyl Alcohol as standard.

Acetic anhydride at 16° C.		Ethyl butyrate at 13° C.		Butyric acid at 13° C.	
Wave-length in microns.	Refractive index.	Wave-length in microns.	Refractive index.	Wave-length in microns.	Refractive index.
·4226	1·4018	·4475	1·4032	·5359	1·4034
·4168	1·4023	·4212	1·4056	·4866	1·4060
·4007	$1·4042_4$	·4020	1·4077	·4651	1·4074
·3985	1·4044	·3978	1·4080	·4587	1·4078
·3759	1·4073	·3923	1·4087	·4508	1·4083
·3676	1·4085	·3860	1·4095	·4378	1·4093
·3618	1·4095	·3688	1·4120	·4260	1·4104
·3547	1·4108	·3618	1·4131	·4178	1·4113
·3493	$1·4117_5$	·3523	1·4150	·4049	1·4129
·3435	1·4131	·3413	1·4169	·3924	1·4144
·3360	1·4147	·3337	1·4184	·3824	1·4157
·3274	1·4164	·3274	1·4198	·3734	1·4169
·3220	1·4174	·3195	1·4219	·3600	1·4188
		·3126	1·4237	·3530	1·4202
		·3063	1·4257	·3464	1·4214
		·3010	1·4272	·3348	1·4241
		·2961	1·4289	·3274	1·4258
		·2883	1·4316	·3195	1·4277
		·2824	1·4338	·3126	1·4298
		·2766	1·4359	·3063	1·4315
				·3010	1·4330
				·2961	1·4346

TABLE I. (*c*).

	Wave-length in microns.	Temperature coefficient of refractive index.
Acetic anhydride	·4500	·00040 per ° C.
	·2961	·00044 „
Ethyl butyrate	·5100	·00041 „
	·3200	·00043 „
Butyric acid	·4560	$\cdot 00040_2$ „
	·3100	$\cdot 00043_2$ „
Normal butyl alcohol .	·4600	·00040 „
	·3200	$\cdot 00043_5$ „

Fig. 1.



Refractive indices.

Magneto-Optical Dispersion.

Acetic Anhydride.

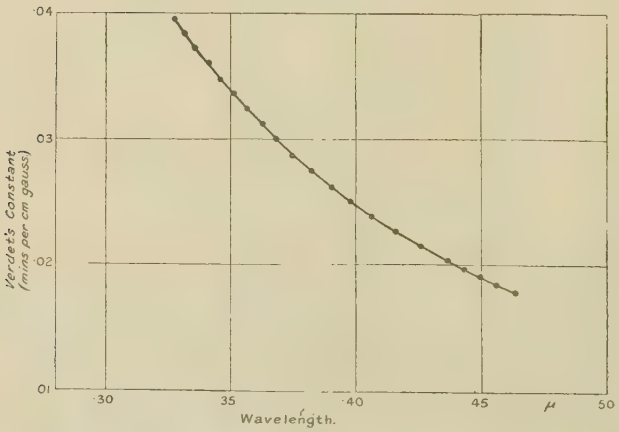
The specimen of acetic anhydride employed for the magneto-optical experiments distilled over between 139·3° C. and 139·8° C. at a pressure of 763 mm. of mercury, its correct normal boiling-point being 139·6° C. The experimental results are given in Table II. (*a*) and fig. 2.

Table II. (*b*) gives a series of values of n, the refractive index, and δ, Verdet's constant, taken from fig. 1 and

TABLE II. (*a*).

Temperature in ° C.	Wave-length in microns.	Verdet's constant in min./cm. gauss.
16	·4633	$\cdot 0180_0$
16	·4563	$\cdot 0186_0$
16·1	·4495	$\cdot 0192_0$
16·1	·4429	$\cdot 0198_0$
16	·4370	$\cdot 0204_0$
16	·4260	$\cdot 0216_0$
16·1	·4158	$\cdot 0228_0$
16	·4065	$\cdot 0240_0$
16	·3975	$\cdot 0252_0$
16	·3897	$\cdot 0264_0$
16	·3820	$\cdot 0276_1$
16	·3743	$\cdot 0288_1$
16	·3679	$\cdot 0300_5$
16	·3621	$\cdot 0312_1$
16·1	·3562	$\cdot 0324_1$
16	·3506	$\cdot 0336_1$
16	·3454	$\cdot 0348_1$
16	·3406	$\cdot 0360_0$
16	·3358	$\cdot 0372_1$
15·9	·3314	$\cdot 0384_1$
15·9	·3274	$\cdot 0396_1$

Fig.



Magnetic rotary dispersion of acetic anhydride at 16° C.

Table II. (*a*) respectively. It was found that the experimental results could be represented by a formula of the type

$$\phi = n\delta\lambda^2 = \mathrm{K}\left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2}\right)^2,$$

and from several pairs of values of ϕ and λ the values of λ_1 and K were obtained.

Table II. (*b*).

	λ in microns.	n.	δ in min./cm. gauss.
(*a*)	·4495	1·3993	$\cdot 0192_0$
(*b*)	·4260	1·4014	$\cdot 0216_0$
(*c*)	·4065	1·4035	$\cdot 0240_0$
(*d*)	·3406	1·4138	$\cdot 0360_0$
(*e*).....	·3314	1·4157	$\cdot 0384_1$

The values of the function ϕ were calculated for each wave-length, and the following pairs used to obtain the constants :—

From (*a*) and (*c*) $\lambda_1 = \cdot 1029\,\mu$ and $\mathrm{K} = 4\cdot 875_4 \times 10^{-3}$.
,, (*b*) ,, (*d*) $\lambda_1 = \cdot 1035\,\mu$,, $\mathrm{K} = 4\cdot 863 \times 10^{-3}$.
,, (*c*) ,, (*e*) $\lambda_1 = \cdot 1030\,\mu$,, $\mathrm{K} = 4\cdot 874_7 \times 10^{-3}$.
,, (*a*) ,, (*e*) $\lambda_1 = \cdot 1031\,\mu$,, $\mathrm{K} = 4\cdot 872_4 \times 10^{-3}$.

The mean values of λ_1 and K are $\cdot 1031\,\mu$ and $4\cdot 871_4 \times 10^{-3}$ respectively, δ being measured in minutes per cm. gauss, and λ in microns.

Thus the equation representing the magneto-optical dispersion of acetic anhydride for the range of the spectrum investigated ($\cdot 4633\,\mu$ to $\cdot 3275\,\mu$) is

$$n\delta = 4\cdot 871_4 \times 10^{-3} \cdot \frac{\lambda^2}{\{\lambda^2 - (\cdot 1031)^2\}^2}.$$

This equation was used to calculate the values of δ for other wave-lengths where experimental determinations had been carried out. The values of n were read off from fig. 1.

The value of δ, calculated from the equation, for sodium light is $\cdot 01072_4$ at 16° C., and assuming that the value of Verdet's constant of water at $\cdot 5893\,\mu$ is ·0131, the specific rotation of acetic anhydride relative to water is $\cdot 818_8$.

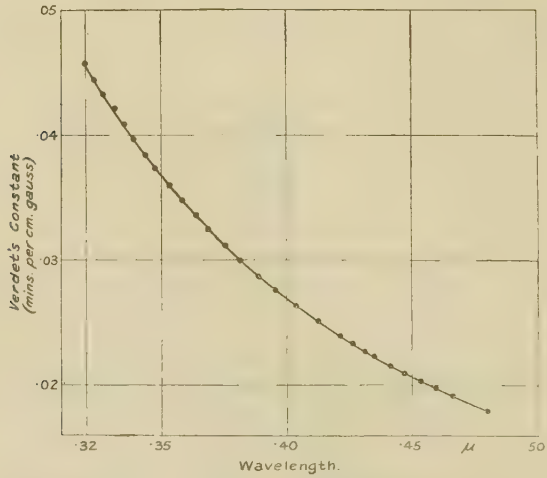
TABLE II. (*c*).

λ (microns).	δ (observed).	δ (calculated).
·4633	$·0180_0$	$·0179_7$
·4563	$·0186_0$	$·0185_8$
·4370	$·0204_0$	$·0204_2$
.4158	$·0228_0$	$·0228_1$
·3897	$·0264_0$	$·0263_9$
·3679	$·0300_5$	$·0301_0$
·3506	$·0336_1$	$·0336_4$
·3358	$·0372_1$	$·0372_2$
·3274	$·0396_1$	$·0395_4$

Normal Butyric Acid.

The butyric acid employed in the determination of Verdet's constant distilled over between 162·3° C. and 162·6° C. at a

Fig. 3.



Magnetic rotary dispersion of butyric acid at 13° C.

pressure of 758 mm. of mercury, its true normal boiling-point being 162·5° C. The experimental results are given in Table III. (*a*) and plotted in fig. 3.

In Table III. (*b*) values of Verdet's constant and the refractive indices corresponding to certain wave-lengths are given. These were employed to calculate the constants of the magneto-optical dispersion equation for butyric acid.

TABLE III. (*a*).

Temperature in ° C.	Wave-length in microns.	Verdet's constant in min./cm. gauss.
13·1	·4802	$·0180_3$
13	·4663	$·0192_3$
13·1	·4593	$·0198_7$
12·9	·4535	$·0204_3$
13·1	·4472	$·0210_8$
13·1	·4419	$·0216_4$
13·2	·4358	$·0223_5$
13·1	·4316	$·0228_4$
13·2	·4265	$·0234_8$
13·1	·4217	$·0240_4$
13·3	·4128	$·0252_4$
13·1	·4041	$·0264_4$
13·1	·3960	$·0276_4$
13·1	·3889	$·0288_6$
13·1	·3818	$·0300_6$
13	·3755	$·0312_6$
13·2	·3683	$·0324_6$
13	·3638	$·0336_7$
13·1	·3585	$·0348_7$
13	·3532	$·0360_7$
13·1	·3483	$·0372_9$
13·1	·3437	$·0384_7$
13	·3393	$·0396_8$
13·1	·3353	$·0408_8$
13·2	·3312	$·0420_8$
13·1	·3272	$·0432_8$
13·1	·3236	$·0444_9$
13·1	·3202	$·0456_9$

TABLE III. (*b*).

	Wave-length in microns.	Verdet's constant.	Refractive index, n.
(*a*)	·4419	$·0216_4$	1·4090
(*b*)	·4041	$·0264_4$	$1·4129_6$
(*c*)	·3638	$·0336_7$	$1·4183_3$
(*d*)	·3272	$·0432_8$	1·4258

From (*a*) and (*b*) $\lambda_1 = ·1065\ \mu$ and $K = 5·28_2 \times 10^{-3}$.
,, (*b*) ,, (*c*) $\lambda_1 = ·1068\ \mu$,, $K = 5·27_7 \times 10^{-3}$.
,, (*c*) ,, (*d*) $\lambda_1 = ·1059\ \mu$,, $K = 5·29_6 \times 10^{-3}$.
,, (*a*) ,, (*d*) $\lambda_1 = ·1063\ \mu$,, $K = 5·28_4 \times 10^{-3}$.

The mean values of λ_1 and K are $\cdot1064\,\mu$ and $5\cdot28_5\times10^{-3}$ respectively, and the equation representing the magneto-optical dispersion of normal butyric acid over the region of the spectrum investigated ($\cdot4802\,\mu$ to $\cdot3208\,\mu$) is

$$n\delta=5\cdot28_5\times10^{-3}\cdot\frac{\lambda^2}{\{\lambda^2-(\cdot1064)^2\}^2}.$$

This equation was used to calculate δ for a few wave-lengths at which experimental determinations had been carried out. The values of n used were read off from fig. 1. Table III. (*c*) shows a comparison of the observed and calculated values.

The equation was also employed to calculate Verdet's constant for sodium light, and the value obtained $=\cdot0116_1$

Table III. (*c*).

λ (in microns).	δ (observed).	δ (calculated).
·4802	$\cdot0180_3$	$\cdot0180_3$
·4535	$\cdot0204_3$	$\cdot0204_4$
·4316	$\cdot0228_4$	$\cdot0228_1$
·4128	$\cdot0252_4$	$\cdot0252_1$
·3818	$\cdot0300_6$	$\cdot0301_0$
·3532	$\cdot0360_7$	$.0360_8$
·3353	$\cdot0408_8$	$\cdot0408_1$
·3202	$\cdot0456_9$	$\cdot0456_3$

at 13·1° C. Perkin * found the specific rotation of butyric acid to be ·8803 at 19·9° C. and ·8826 at 18° C. Assuming the temperature coefficient deduced from these results, the value of the specific rotation at 13° C. is ·888, and taking the value of Verdet's constant of water for sodium light to be ·0131, the value deduced from Perkin's results is ·01163. This compares satisfactorily with the value $\cdot0116_1$ calculated from the equation.

Lowry and Dickson †, who determined the magnetic rotations of butyric acid for a number of wave-lengths in the visible spectrum, have compared the rotary powers at various wave-lengths with that at $\lambda=\cdot5461\,\mu$. A comparison of their results with those calculated from the magneto-optical dispersion equation, which represents the present results, is given in Table III. (*d*).

* Journ. Chem. Soc. i. p. 483 (1884).
† Journ. Chem. Soc. ciii. p. 1067 (1913).

TABLE III. (*d*).

Wave-length in microns.	Magnetic rotary power relative to that at ·5461 μ.	
	Lowry and Dickson.	Present results.
·6708	·645	·647
·5893	·853	·850
·4359	1·634	1·634

Normal Ethyl Butyrate.

The ethyl butyrate employed for the determination of the magneto-optical rotations distilled over at the correct normal

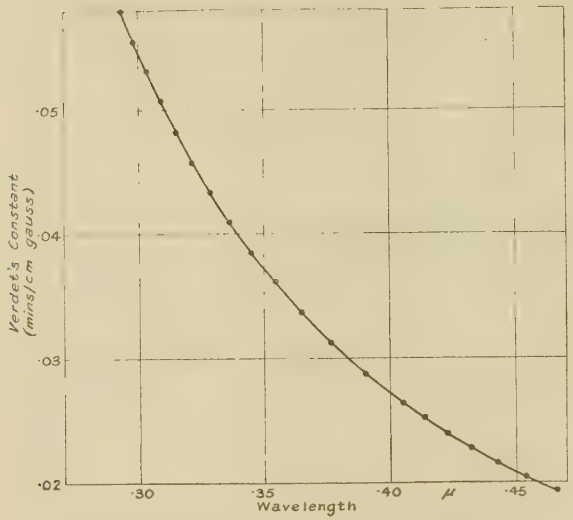
TABLE IV. (*a*).

Temperature in ° C.	Wave-length in microns.	Verdet's constant in min./cm. gauss.
12·9	·4669	$·0192_3$
13·3	·4542	$·0204_3$
13·1	·4427	$·0216_3$
13·2	·4320	$·0228_4$
13	·4224	$·0240_4$
13·1	·4134	$·0252_4$
13·1	·4050	$·0264_4$
13·1	·3899	$·0288_6$
13·1	·3763	$·0312_6$
13·1	·3648	$·0336_7$
13·2	·3541	$·0360_7$
13·2	·3445	$·0384_7$
13·1	·3360	$·0408_8$
13·1	·3282	$·0432_8$
13·1	·3210	$·0456_9$
13·1	·3144	$·0480_9$
13·1	·3082	$·0505_0$
13·1	·3026	$·0529_0$
13·1	·2973	$·0553_1$
13·1	·2925	$·0577_2$

boiling-point 121·4° C. when the pressure was 761 mm. of mercury. The experimental results are given in Table IV. (*a*) and fig. 4.

Table IV. (*b*) contains results read off from fig. 1 and Table IV. (*a*), and these were made use of in solving the magneto-optical dispersion equation.

Fig. 4.



Magnetic rotary dispersion of ethyl butyrate at 13° C

TABLE IV. (*b*).

	Wave-length in microns.	Refractive index, *n*.	Verdet's constant in min./cm. gauss.
(*a*)	·4427	1·4036	$·0216_3$
(*b*).....	·3763	1·4110	$·0312_6$
(*c*).....	·3541	$1·4146_4$	$·0360_7$
(*d*)	·2925	1·4299	$·0577_2$

From (*a*) and (*b*) $\lambda_1 = ·1073\ \mu$ and $K = 5·272 \times 10^{-3}$.
„ (*a*) „ (*c*) $\lambda_1 = ·1080_3\ \mu$ „ $K = 5·262 \times 10^{-3}$.
„ (*b*) „ (*d*) $\lambda_1 = ·1086\ \mu$ „ $K = 5·249 \times 10^{-3}$.
„ (*c*) „ (*d*) $\lambda_1 = ·1085\ \mu$ „ $K = 5·252 \times 10^{-3}$.
„ (*a*) „ (*d*) $\lambda_1 = ·1082_4\ \mu$ „ $K = 5·260 \times 10^{-3}$.

The mean value of $\lambda_1 = ·1081\ \mu$ and $K = 5·25_9 \times 10^{-3}$, and the equation representing the magneto-optical dispersion of ethyl butyrate over the region ·4669 μ to ·2925 μ is

$$n\delta = 5·25_9 \times 10^{-3} \frac{\lambda^2}{\{\lambda^2 - (·1081)^2\}^2}.$$

The accuracy of the representation of the results by the equation is shown in Table IV. (*c*), where a comparison is

made of the experimental values of Verdet's constant and the values calculated from the equation.

TABLE IV. (*c*).

λ (microns).	δ (observed).	δ (calculated).
·4669	$·0192_3$	$·0192_1$
·4224	$·0240_4$	$·0240_2$
·3648	$·0336_7$	$·0336_2$
·3360	$·0408_8$	$·0408_7$
·3210	$·0456_9$	$·0456_7$
·3026	$·0529_t$	$·0529_0$
·2973	$·0553_1$	$·0553_1$

The value of Verdet's constant for sodium light calculated from the above equation is $·0116_2$ at 13·1° C. Perkin* has measured the specific rotation of ethyl butyrate relative to water, and found the value to be ·8889 at 13° C. Taking the value of Verdet's constant for water to be ·0131, the value of Verdet's constant for ethyl butyrate at 13° C. is ·01164. This is in good agreement with the value calculated above.

The Natural Dispersion Equations.

The experimental results have shown that the magneto-optical dispersion of each liquid over the range of the spectrum investigated can be explained by the presence of a single absorption band. A satisfactory natural dispersion equation can be obtained for each of these liquids if the assumption is now made that the same absorption band is responsible for the natural dispersion of the liquid over the same range of wave-length.

The constants of the equation of the form

$$n^2-1=b_0+\frac{b_1}{\lambda^2-\lambda_1^2}$$

can be obtained from two values of the refractive index corresponding to two wave-lengths.

Acetic Anhydride.

The mean values of b_1 and b_0 are $·921_3\times10^{-10}$ and $·9101_8$ respectively, and the natural dispersion equation of acetic anhydride is

$$n^2=1·9101_8+\frac{·921_3\times10^{-10}}{\lambda^2-(1·031\times10^{-5})^2}.$$

* Journ. Chem. Soc. i. p. 499 (1884).

The pairs of values used are given below :—

TABLE V. (*a*).

λ (cm.×10⁵).	*n*.	b_1.	b_0.
6·678 4·226	1·3897 $1{\cdot}4017_8$	$\cdot922_2\times10^{-10}$	$\cdot9100_3$
5·016 3·493	1·3959 $1{\cdot}4117_5$	$\cdot921_7\times10^{-10}$	$\cdot9102_9$
4·472 3·220	$1{\cdot}3995_5$ 1·4174	$\cdot920_0\times10^{-10}$	$\cdot9101_6$

This equation was used to calculate n for a number of wave-lengths where experimental values had been obtained. Table V. (*b*) contains a comparison of the calulated and experimental values.

TABLE V. (*b*).

λ (microns).	*n* (observed).	*n* (calculated).
·5876	1·3920	1·3920
4922	1·3966	1·3964
·4713	1·3978	$1{\cdot}3977_7$
·4168	1·4023	1·4024
·3985	1·4044	1·4044
·3547	$1{\cdot}4107_6$	$1{\cdot}4107_4$
·3435	1·4131	1·4128
·3274	1·4164	1·4162

Butyric Acid.

The constants b_1 and b_0 of the natural dispersion equation for butyric acid were calculated from the pairs of values given in the following table :—

TABLE VI. (*a*).

λ (cm.×10⁵).	*n*.	b_1.	b_0.
6·678 4·508	1·3988 1·4083	$\cdot916_5\times10^{-10}$	$\cdot9355_6$
5·876 3·924	1·4011 1·4144	$\cdot932_6\times10^{-10}$	$\cdot9351_6$
5·016 3·530	1·4051 1·4202	$\cdot914_5\times10^{-10}$	$\cdot9362_6$
4·713 3·010	1·4070 1·4330	$\cdot938_3\times1^{-1}$	$\cdot9351_4$
4·472 2·961	1·4086 1·4346	$\cdot948_1\times10^{-10}$	$\cdot9339_1$

The mean value of $b_1 = \cdot 930_0 \times 10^{-10}$ and of $b_0 = \cdot 9352_0$, and the equation representing the natural dispersion of butyric acid is

$$n^2 = 1 \cdot 9352_0 + \frac{\cdot 930_0 \times 10^{-10}}{\lambda^2 - (1 \cdot 064 \times 10^{-5})^2}.$$

Values of n calculated from this equation are compared in Table VI. (*b*). with the observed values at certain wavelengths.

TABLE VI. (*b*).

λ (microns).	n (observed).	n (calculated).
·5359	1·4034	1·4032
·4922	1·4057	1·4055
·4651	1·4074	1·4073
·4178	1·4113	1·4114
·3734	1·4169	1·4170
·3464	1·4214	1·4216
·3274	1·4258	1·4256
·3063	1·4315	1·4311

Ethyl Butyrate.

The following pairs of values of the refractive indices were used in calculating the constants of the natural dispersion equation for ethyl butyrate :—

TABLE VII. (*a*).

λ (cm. $\times 10^5$).	n.	b_1.	b_0.
6·678 4·020	$1 \cdot 3936_6$ 1·4077	$\cdot 900_6 \times 10^{-10}$	$\cdot 9215_5$
5·876 3·618	$1 \cdot 3958_2$ 1·4131	$\cdot 900_5 \times 10^{-10}$	$\cdot 9213_2$
5·016 3·126	1·3996 1·4237	$\cdot 912_6 \times 10^{-10}$	$\cdot 9208_4$
4·713 2·824	1·4015 1·4338	$\cdot 921_3 \times 10^{-10}$	$\cdot 9204_2$
4·472 2·766	$1 \cdot 4032_5$ 1·4359	$\cdot 916_3 \times 10^{-10}$	$\cdot 9204_5$

The mean values of b_1 and b_0 are $\cdot 910_3 \times 10^{-10}$ and $\cdot 9209_2$ respectively, and the natural dispersion equation is

$$n^2 = 1 \cdot 9209_2 + \frac{\cdot 910_3 \times 10^{-10}}{\lambda^2 - (1 \cdot 081 \times 10^{-5})^2}.$$

Table VII. (*b*) contains a comparison of the observed results at certain wave-lengths and the values calculated from the above equation.

Table VII. (*b*).

λ (microns).	n (observed).	n (calculated).
·4922	$1{\cdot}4002_5$	$1{\cdot}4001_4$
·4475	1·4032	1·4033
·3860	1·4095	1·4097
·3413	1·4169	1·4170
·3274	1·4198	1·4199
·3063	1·4257	1·4255
·2961	1·4289	1·4286

Calculation of $\frac{e}{m}$.

As pointed out in the introduction, the value of $\frac{e}{m}$ can be obtained from the relation

$$\frac{e}{m} = -\frac{2C^2K}{b_1}.$$

The values of K given in this paper have been calculated when δ is expressed in minutes per cm. gauss and λ in microns. For the purpose of evaluating $\frac{e}{m}$ from the above equation the values of K must be calculated when δ is expressed in radians per cm. gauss and λ in cm.

The absolute values of K for acetic anhydride, butyric acid, and ethyl butyrate are $1{\cdot}417 \times 10^{-14}$, $1{\cdot}537_3 \times 10^{-14}$, and $1{\cdot}529_8 \times 10^{-14}$ respectively. The corresponding values of b_1 are $\cdot 921_3 \times 10^{-10}$, $\cdot 930_0 \times 10^{-10}$, and $\cdot 910_3 \times 10^{-10}$. On substituting these in the above equation the calculated values of $\frac{e}{m}$ for acetic anhydride, butyric acid, and ethyl butyrate are $\cdot 923 \times 10^7$, $\cdot 992 \times 10^7$, and $1{\cdot}00_8 \times 10^7$ e.m.u. respectively.

Discussion of Results.

The magneto-optical dispersion of acetic anhydride, butyric acid, and ethyl butyrate over the range of the spectrum extending from about ·46 μ to about ·30 μ can be represented by the equation

$$n\delta = K \cdot \frac{\lambda^2}{\{\lambda^2 - \lambda_1^2\}^2},$$

where δ and n are the values of Verdet's constant and the refractive index of the liquid for a wave-length λ, K a constant which varies from liquid to liquid, and λ_1 the wave-length corresponding to the free period of the resonators. It is of interest to compare the values of K and λ_1 for butyric acid and ethyl butyrate with those obtained by Stephens and Evans * and Jenkins and Evans † for propionic acid and some of its esters. These results are collected in Table VIII. The magneto-optical rotations of acetic acid and formic acid in the ultra-violet region of the spectrum have not yet been examined in this laboratory, and unpublished results on the magneto-optical rotation of propyl acetate suggest the necessity of repeating with greater accuracy the previous results of Evans and Evans ‡ on

TABLE VIII.

Liquid.	Molecular weight.	λ_1 (microns).	K.	Temp. in °C.
Propionic acid..... (C_2H_5 . COOH)	74	·1051	$5{\cdot}00_8\times10^{-3}$	13
Methyl propionate ... (C_2H_5 . $COOCH_3$)	88	·1066	$4{\cdot}77_1\times10^{-3}$	17·1
Ethyl propionate..... (C_2H_5 . $COOC_2H_5$)	102	·1075	$5{\cdot}06_8\times10^{-3}$	15·8
Butyric acid..... (C_3H_7 . COOH)	88	·1064	$5{\cdot}28_5\times10^{-3}$	13·1
Ethyl butyrate..... (C_3H_7 . $COOC_2H_5$)	116	·1081	$5{\cdot}25_9\times10^{-3}$	13·1

methyl and ethyl acetates. These substances are now being investigated, and the comparison of the results for similar compounds can then be extended.

An examination of the above table shows that, in general, values of λ_1 increase with increasing molecular weight, the value for propionic acid being ·0013 μ below that of butyric acid, the next member of the homologous series. It is interesting to note that the value of λ_1 for butyric acid is practically the same as that for methyl propionate, which has the same molecular weight.

The value of K is greater for butyric acid than for propionic acid, and the same is true when ethyl and methyl propionates are compared. It is, however, seen that the

* *Loc. cit.*
† Phil. Mag. xi. pp. 377–396 (Feb. 1931).
‡ Phil. Mag. viii. (August 1929).

increase of molecular weight in passing from propionic acid to methyl propionate and in passing from butyric acid to ethyl butyrate is accompanied by a diminution in the value of K.

The natural dispersion of three liquids over the range of spectrum extending from ·6678 μ to ·2800 μ is represented within experimental error by an equation of the type

$$n^2-1=b_0+\frac{b_1}{\lambda^2-\lambda_1{}^2},$$

where λ_1 is the wave-length of the absorption band calculated from the magneto-optical experiments, and b_0, b_1 are constants, which vary from liquid to liquid.

A comparison of the values of b_0 and b_1 for the liquids included in Table VIII. are given in Table IX. The values of $\frac{e}{m}$ are also included in the same table.

TABLE IX.

Liquid.	b_0.	$b_1\times10^{10}$.	$\frac{e}{m}$(e.m.u.).
Propionic acid	·9042	·8716	$1\cdot00\times10^7$
Methyl propionate	·8717	·8680	$\cdot96\times10^7$
Ethyl propionate	·8918	·8990	$\cdot99\times10^7$
Butyric acid	·9352	·9300	$\cdot99_2\times10^7$
Ethyl butyrate	·9209	·9103	$1\cdot00_8\times10^7$

An examination of the table shows that, if the two acids are compared, the values of b_0 and b_1 increase with increasing molecular weight, and also that the value of $\frac{e}{m}$ tends to diminish as the molecular weight increases. If the esters are compared, the values of b_0, b_1, and $\frac{e}{m}$ increase with increasing molecular weight. The replacement of hydrogen in propionic acid by the CH_3 group to form methyl propionate reduces the value of $\frac{e}{m}$, and the replacement of hydrogen in butyric acid by the C_2H_5 group slightly increases the value of $\frac{e}{m}$.

From the values of $\frac{e}{m}$ deduced in the present experiments on acetic anhydride, butyric acid, and ethyl butyrate, it can be seen that the resonators controlling the magneto-optical

dispersion in the visible and ultra-violet regions of the spectrum are the electrons. However, the values obtained for $\frac{e}{m}$ are much lower than the accepted value $1{\cdot}77 \times 10^7$ e.m.u.

Summary.

1. The magneto-optical dispersion of acetic anhydride, normal butyric acid, and normal ethyl butyrate in the visible and ultra-violet regions of the spectrum ($\cdot 46\,\mu$ to about $\cdot 30\,\mu$) can be represented by equations of the type

$$n\delta = \mathrm{K} \cdot \frac{\lambda^2}{(\lambda^2 - \lambda_1^2)^2},$$

where δ is Verdet's constant, n the refractive index for wave-length λ, K a constant, and λ_1 the wave-length of the absorption band.

The values of λ_1 for acetic anhydride, butyric acid, and ethyl butyrate are $\cdot 1031\,\mu$, $\cdot 1064\,\mu$, and $\cdot 1081\,\mu$ respectively.

2. The natural dispersion of acetic anhydride, butyric acid, and ethyl butyrate in the visible and ultra-violet regions of the spectrum ($\cdot 6678\,\mu$ to about $\cdot 2800\,\mu$) can be represented within experimental error by equations of the type

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

where b_0 and b_1 are constants and λ_1 has for each liquid the value determined from the magneto-optical dispersion experiments.

3. The values of $\frac{e}{m}$ for acetic anhydride, butyric acid, and ethyl butyrate, calculated from the results of the magneto-optical and natural dispersion experiments, are $\cdot 923 \times 10^7$, $\cdot 992 \times 10^7$, and $1{\cdot}00_8 \times 10^7$ e.m.u. respectively.

July 1931.

XXI. *Activities and the Standard State.*—I. *Activity Coefficients.* *By* Angus Macfarlane, *B.A.*, *and* Oliver Gatty, *B.A.**

THE concentrations of solutions have been variously expressed in terms of a given volume or weight either of solvent or solution. For dilute aqueous solutions there is

* Communicated by Sir Harold Hartley, F.R.S.

no appreciable difference between concentrations measured on the weight or the volume normality scale. But in other solvents, where the density is not unity, this is no longer the case, and, in consequence, confusion has sometimes arisen in investigations of the thermodynamical properties of solutions. This paper and the following one deal with the choice of suitable concentration scales when the free energy contents of solutions are to be considered.

Since only differences in free energy can be measured, the partial molal free energy of a solute in solution at a given temperature and pressure is defined by reference to a standard state. For convenience in correlating the partial molal free energies of a solute in different solvents, this standard state should be so chosen as to be independent of the nature of the medium. This was done by G. N. Lewis, in dealing with fugacities, which he referred to the rarefied vapour of the pure solute. The term fugacity will be employed in what follows as simply implying any absolute standard of this type. In practice the simplest fugacity system would take as the standard the pure solute at a given temperature, but reference even to this is difficult owing to our general ignorance of the properties of saturated solutions. In consequence, free energies are referred to a separate standard state for each solvent. The activities a_1 and a_2 of a solute in any one solvent at two concentrations are related to the partial molal free energies by the expression

$$\overline{F}_2 - \overline{F}_1 = RT \, ln \frac{a_2}{a_1}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

An activity so defined can be related to a fugacity, α, and to the fugacity of the solute in the standard state, α_0, by the expression

$$a = \frac{\alpha}{\alpha_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since all solutions approach ideal behaviour at very high dilutions, the standard state is usually chosen so that

$$\underset{c \to 0}{\mathrm{Lt}} \frac{a}{c} = 1.$$

But this standard state is dependent on the concentration scale selected which may be any one of six that have been used from time to time. Thus the concentration of a given solution may be expressed in :—

(1) Gram molecules of solute per 1000 c.c. of solution.

(2) Gram molecules of solute per 1000 c.c. of solvent.

(3) Gram molecules of solute per 1000 gm. of solution.

(4) Gram molecules of solute per 1000 gm. of solvent.

(5) Gram molecules of solute per gram molecule of solution (*i. e.*, molar fraction).

(6) Gram molecules of solute per gram molecule of solvent.

Let the concentrations on these six scales be denoted by c, c', m, m', x, and x' respectively, and the activites by

(1) $a_c = fc$; (2) $a_{c'} = f'c'$; (3) $a_m = \gamma m$;

(4) $a_{m'} = \gamma' m'$; (5) $a_x = \xi x$; (6) $a_{x'} = \xi' x'$;

where f, f', γ, γ', ξ, and ξ' are the activity coefficients, and the six standard states are chosen so that

$$\begin{array}{lll} \underset{c\to 0}{\mathrm{Lt}}\,\frac{a_c}{c} = 1\,; & \underset{m\to 0}{\mathrm{Lt}}\,\frac{a_m}{m} = 1\,; & \underset{x\to 0}{\mathrm{Lt}}\,\frac{a_x}{x} = 1\,; \\ \underset{c'\to 0}{\mathrm{Lt}}\,\frac{a_{c'}}{c'} = 1\,; & \underset{m'\to 0}{\mathrm{Lt}}\,\frac{a_{m'}}{m'} = 1\,; & \underset{x'\to 0}{\mathrm{Lt}}\,\frac{a_{x'}}{x'} = 1\,; \end{array} \quad . \quad (3)$$

The various concentration units used are simply related to each other :—

$$\left.\begin{array}{ll} \frac{c}{m} = \Delta_s, & \text{where } \Delta_s = \text{the density of the solution.} \\ \frac{c'}{m'} = \Delta, & \text{where } \Delta = \text{the density of the solvent.} \\ \frac{m}{m'} = \frac{1000}{1000+\mathrm{W}}, & \text{where W = the number of grams of solute dissolved per 1000 gms. of solvent.} \\ \frac{c}{c'} = \frac{1000}{1000+\mathrm{V}}, & \text{where V = the volume change after the addition of W gm. of solute to 1000 c.c. of solvent.} \\ \frac{x}{x'} = 1-x. & \\ \frac{m'}{x'} = \frac{1000}{\mathrm{M}}, & \text{where M = the molecular weight of the solvent.} \end{array}\right\} \quad . \quad (4)$$

The properties of the solution tend towards those of the

pure solvent at low concentrations, and it is clear from expression (4) that

$$\underset{c\to 0}{\mathrm{Lt}}\,\frac{c}{c'}=1\,;\qquad \underset{m\to 0}{\mathrm{Lt}}\,\frac{m}{m'}=1\,;\qquad \mathrm{Lt}\,\frac{x}{x'}=1. \quad . \quad (5)$$

Thus it follows in the limit that

$$\underset{c\to 0}{\mathrm{Lt}}\left[\frac{\alpha}{\alpha_{0_c}}=a_c=c=c'=a_{c'}=\frac{\alpha}{\alpha_{0_{c'}}}\right],$$

and therefore

$$\alpha_{0_c}=\alpha_{0_{c'}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

similarly

and

$$\left.\begin{aligned}\alpha_{0_m}&=\alpha_{0_{m'}}\\ \alpha_{0_x}&=\alpha_{0_{x'}}\end{aligned}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus it is seen that for any solvent the concentration scales (1) and (2) lead to the same standard state; the scales (3) and (4) both lead to another, and scales (5) and (6) to yet a third. Therefore the following equations hold for a given solution *at all concentrations* :—

$$\left.\begin{aligned}a_c&=a_{c'},\\ a_m&=a_{m'},\\ a_x&=a_{x'},\end{aligned}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and from equation (4)

$$\left.\begin{aligned}\frac{f'}{f}&=\frac{1000}{1000+\mathrm{V}},\\ \frac{\gamma'}{\gamma}&=\frac{1000}{1000+\mathrm{W}},\end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that the activity coefficients of a given solution will differ according to whether the concentration scale refers to the solvent or the solution.

When a solution in which the solute has fugacity α is considered, the standard states and activity coefficients on the weight, volume, and molecular fraction scales can be related to each other by a similar type of reasoning.

$$\underset{m\to 0}{\mathrm{Lt}}\;a_m\equiv\gamma m\equiv\frac{\alpha}{\alpha_{0_m}}=m,$$

$$\underset{c\to 0}{\mathrm{Lt}}\;a_c\equiv f.c\equiv\frac{\alpha}{\alpha_{0_c}}=c,$$

$$\underset{x\to 0}{\mathrm{Lt}}\ a_x \equiv \xi x \equiv \frac{\alpha}{\alpha_{0_x}} = x,$$

$$\underset{m\to 0}{\mathrm{Lt}}\ \frac{c}{m} = \Delta \quad \text{and} \quad \underset{m\to 0}{\mathrm{Lt}}\ \frac{m}{x} = \frac{1000}{\mathrm{M}}.$$

$$\therefore \qquad \Delta = \frac{\alpha_{0_m}}{\alpha_{0_c}} = \frac{a_c}{a_m} = \frac{a_{c'}}{a_{m'}} \quad (\textit{at all concentrations}), \qquad (10)$$

and

$$\frac{1000}{\mathrm{M}} = \frac{\alpha_{0_x}}{\alpha_{0_m}} = \frac{a_m}{a_x} = \frac{a_{m'}}{a_x} \quad (\textit{at all concentrations}). \qquad (11)$$

Now from the definition of the activity coefficients it is evident, since

$$\frac{c'}{m'} = \Delta \quad \text{and} \quad \frac{m'}{x'} = \frac{1000}{\mathrm{M}} \quad \textit{at all concentrations},$$

that

$$f' = \gamma' = \xi'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

So that activity coefficients when referred to concentration scales (2), (4), or (6) are always the same. At finite concentrations this relationship does not hold for concentration scales (1), (3), and (5).

Equations (6), (7), and (8) show that the standard state is dependent on the unit of concentration employed, but is independent of whether these units refer to the solvent or to the solution ; while equation (12) gives a strong reason for using a concentration scale that refers to the solvent rather than the solution. It is customary to look on the activity coefficient as a property of a solution which measures its departure from the ideal. If so, an activity coefficient that is independent of the units of concentration is desirable so that it may really be said to be a property of the solution. It is accordingly suggested that the concentration scales employed when determining activity coefficients should refer to the solvent rather than the solution. In dilute solutions, of course, the difference is negligible.

The Debye-Hückel * expression represents the electrical contribution to the work function A (constant volume function) of the solution. Since it is only valid in regions where it may be equated to the true free energy F without appreciable error, they were able to deduce an equation for the activity coefficient of the solute which was necessarily in

* Debye and Hückel, *Phys. Zeit.* xxiv. pp. 185, 305 (1923).

terms of c. This expression can only be expected to hold in solutions more dilute than hundredth normal, in which range concentrations calculated in terms of quantity of solvent or of solution are practically indistinguishable. But equation (12) shows that only activity coefficients referred to the solvent basis have a simple physical significance in strong solution. To avoid the use of separate scales for dilute and concentrated solutions, it is therefore suggested that the c' unit of concentration be employed. This scale has the additional advantage, when testing the theory in non-aqueous solutions, of being ascertainable without a knowledge of the density of the solution.

By referring the concentration to the solvent and not to the solution it is possible to examine the temperature and pressure coefficients of the activity coefficients for a solution of constant composition. A more detailed analysis of Bjerrum's equation for the heats of dilution can be made by this means, and the method leads eventually to expressions for the fugacity in the standard state as a function of pressure and temperature.

Consider a solution containing N_1 gram molecules of solvent and N_2 of solute. From ordinary thermodynamics the partial molal heat-content and volume of the solute in any such solution may be calculated from the following equations:

$$\left(\frac{\partial \ln \alpha}{\partial T}\right)_{p,\,N} = -\frac{\bar{H}}{RT^2}, \quad \ldots \quad (13)$$

$$\left(\frac{\partial \ln \alpha}{\partial p}\right)_{T,\,N} = \frac{\bar{V}}{RT}, \quad \ldots \quad (14)$$

where the subscript N implies that both N_1 and N_2 are kept constant. The equations hold also for a solution which is in the standard state at the initial temperature and pressure, but after any infinitesimal change in these variables the solution does not necessarily correspond to the standard state in the new conditions. Thus, although these equations give the partial molal heat-content and volume of the solute in a solution which is a standard at the given temperature and pressure, information of the change of standard state with temperature and pressure must be obtained by an indirect method.

Let a_1 and a_2 be the activities of the solute at concentrations 1 and 2 on any scale. Then the ratios $\frac{a_2}{a_1}$ and $\frac{c_2'}{c_1'}$

can be determined without reference to the standard state. Accordingly the ratio $\frac{f_2'}{f_1'}$ is independent of any knowledge of the standard state and we may write

$$\left(\frac{\partial\, ln\, a_2/a_1}{T}\right)_{p,N} = \left(\frac{ln\, \alpha_2/\alpha_1}{T}\right)_{p,N}$$

$$= \left(\frac{ln\, c_2'/c_1'}{T}\right)_{p,N} + \left(\frac{ln f_2'/f_1'}{T}\right) = \frac{\bar{H}_1 - \bar{H}_2}{RT^2}.$$

A similar set of equations holds for all the other concentration scales. Only on the volume scale is the concentration a function of temperature and pressure, but by reference to the volume of pure solvent the concentration ratio $\frac{c_2'}{c_1'}$ is independent of these variables, although the ratio $\frac{c_2}{c_1}$ is not. Therefore

$$\left(\frac{\partial\, ln f_2'/f_1'}{\partial T}\right)_{p,N} = \left(\frac{\partial\, ln\, \gamma_2'/\gamma_1'}{\partial T}\right)_{p,N}$$

$$= \left(\frac{\partial\, ln\, \xi_2'/\xi_1'}{\partial T}\right)_{p,N} = \frac{\bar{H}_1 - \bar{H}_2}{RT^2},$$

since, by equation (12), $f' = \gamma' = \xi'$ at all temperatures, pressures, and concentrations.

Now let f_2' refer to any solution that is at a limitingly great dilution. Then f_2' is sensibly equal to unity at all temperatures and H_2 becomes $H_{c=0}$, which has a constant value at all limitingly low concentrations. Equation (14) then becomes

$$-\left(\frac{\partial\, ln f'}{\partial T}\right)_{p,N} = \frac{H - \bar{H}_{c=0}}{RT^2}, \quad . \quad . \quad . \quad (15)$$

and there are two corresponding equations for γ' and ξ'. Thus $-RT^2\left(\frac{ln f'}{T}\right)_{p,N}$ gives the partial molal heat of dilution of the solute to infinite dilution, and the expression is independent of the concentration units employed as long as they refer to the pure solvent and not to the solution. This result must hold at any concentration.

Similarly, by differentiating with respect to pressure, it is found that

$$\left(\frac{ln f'}{p}\right)_{T,N} = \frac{V - \bar{V}_{c=0}}{RT}, \quad . \quad . \quad . \quad . \quad (16)$$

where V is the partial molal volume of the solute at concentration c and $\bar{V}_{c=0}$ its value at infinite dilution. This result is also independent of the concentration units and holds at any concentration.

Returning now to solutions in the standard state, the variation of the fugacities may be examined to find whether their concentrations also depend on the temperature and pressure. Since

$$\left.\begin{aligned} \alpha_{0_c} &= \frac{\alpha}{c'f'}, \\ \alpha_{0_m} &= \frac{\alpha}{m_0'\gamma'}, \\ \alpha_{0_x} &= \frac{\alpha}{x_0'.\xi'}, \end{aligned}\right\} \quad \ldots\ldots (17)$$

$$\begin{aligned} \left(\frac{\partial ln\,\alpha_{0_c}}{\partial T}\right)_p &= \left(\frac{\partial ln\,\alpha}{\partial T}\right)_{p,N} - \left(\frac{\partial ln\,c'}{\partial T}\right)_{p,N} - \left(\frac{\partial ln\,f'}{\partial T}\right)_{p,N} \\ &= -\frac{\bar{H}}{RT^2} - \left(\frac{\partial ln\,c'}{\partial T}\right)_{p,N} + \frac{\bar{H}-\bar{H}_{c=0}}{RT^2} \\ &= -\frac{\bar{H}_{c=0}}{RT^2} - \left(\frac{\partial ln\,c'}{\partial T}\right)_{p,N} \\ &= -\frac{\bar{H}_{c=0}}{RT^2} + \left(\frac{\partial ln\,V}{\partial T}\right)_{p,N}, \quad \ldots\ldots (18) \end{aligned}$$

where V is the molal volume of the solvent.

Similarly, since m' and x' are independent of T,

$$\left(\frac{ln\,\alpha_{0_m}}{T}\right)_p = -\frac{\bar{H}_{c=0}}{RT^2}, \quad \ldots\ldots (19)$$

$$\left(\frac{ln\,\alpha_{0_x}}{\partial T}\right)_p = -\frac{H_{c=0}}{RT^2}, \quad \ldots\ldots (20)$$

while, for the pressure variation, the expressions are :

$$\left(\frac{\partial ln\,\alpha_{0_c}}{\partial p}\right)_T = \frac{V_{c=0}}{RT} + \left(\frac{\partial ln\,V}{\partial p}\right)_{T,N}, \quad \ldots (21)$$

$$\left(\frac{\partial ln\,\alpha_{0_m}}{\partial p}\right)_T = \frac{V_{c=0}}{RT} = \left(\frac{\partial ln\,\alpha_{0_x}}{\partial p}\right)_T. \quad \ldots (22)$$

Since $V_{c=0}$ is not in general equal to V, nor $H_{c=0}$ to $\bar{H}$, it is clear, on comparing equations (13) and (14) with (18)

to (20) and (21) to (22) respectively, that the actual concentrations of the solutions in the standard states c_0', m_0', x_0', which, of course, are the reciprocals of the activity coefficients, are functions of both the pressure and temperature of the system. Thus, for a given temperature and pressure, α_0 is completely determined, but α is a function of the concentration as well.

Summary.

The relationships between the standard states and activity coefficients of a solute in solution have been investigated for a number of concentration scales. It is recommended that the concentration should be expressed in gram-molecules of salt in a fixed quantity of solvent. The physical interpretation of the activity coefficient is thereby simplified, while definite relationships can be obtained between it and the partial molal heat and volume of dilution of the solute to infinite dilution. The concentration of solute in the standard states is, in general, a function of the temperature and pressure of the solution. When testing the Debye-Hückel expression in solvents whose density is not unity, a volume normality scale should be used.

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XXII. *Activities and the Standard State.*—II. *Electrode Potentials. By* Oliver Gatty, *B.A., and* Angus Macfarlane, *B.A.**

THE potential difference between an element and a solution of its ions which are at unit activity, *i. e.*, in the standard state, is defined as its single electrode potential. In the preceding paper it was shown in equations (6) and (7) that the standard state is the same whether the concentration unit refers to quantity of solvent or of solution, but in equations (10) and (11) that it is dependent on whether a weight, volume, or molecular scale is chosen. This choice will correspondingly affect the single electrode potentials.

Thus, if π is the electrostatic potential in volts of an

* Communicated by Sir Harold Hartley, F.R.S.

element in contact with a solution of its ions, whose activity is a_m on the weight and a_c on the volume scale,

$$\pi = \pi_{0_c} + \frac{RT}{n\mathbf{F}} \ln a_c$$

$$= \pi_{0_m} + \frac{RT}{n\mathbf{F}} \ln a_m. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Therefore, from equation (10),

$$\pi_{0_m} - \pi_{0_c} = \frac{RT}{n\mathbf{F}} \ln \Delta, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where π_{0_m} and π_{0_c} are the standard single potentials on the two scales, Δ is the density of the solvent, n is the valency of the ion, and $\mathbf{F}$ the value of the Faraday in coulombs.

Since the exact magnitude of the absolute zero of potential is still uncertain, electrode potentials are referred to the standard hydrogen electrode, where hydrogen gas at atmospheric pressure is in equilibrium with a solution containing hydrogen ions at unit activity. The standard electrode potential of an element A, which gives rise to anions in solution, can be calculated from measurements of the e.m f., E_1, of the cell :

$$H_2 \qquad HA \qquad A,$$
$$a_c \text{ or } a_m$$
(1 atmosphere),

since

$$E_1 = {}^{A}\pi_{0_c} - \frac{RT}{\mathbf{F}} \ln a_c^- - \left[{}^{H_2}\pi_{0_c} + \frac{RT}{\mathbf{F}} \ln a_c^+ \right]$$

$$= {}^{A}\pi_{0_m} - \frac{RT}{\mathbf{F}} \ln a_m^- - \left[{}^{H_2}\pi_{0_m} + \frac{RT}{\mathbf{F}} \ln a_m^+ \right]. \quad . \quad (25)$$

But, by definition, ${}^{A}\pi_0 - {}^{H_2}\pi_0$ is the standard electrode potential of the anion, and if the product $a_+ . a_-$ is denoted by $a_\pm^2$, equation (25) may be rewritten :

$$E_1 = {}^{A}\text{E.P.}_c - \frac{2RT}{\mathbf{F}} \ln a_{\pm_c}$$

$$= {}^{A}\text{E.P.}_m - \frac{2RT}{\mathbf{F}} \ln a_{\pm_m}; \quad . \quad . \quad . \quad (26)$$

$$\therefore \quad {}^{A}\text{E.P.}_c - {}^{A}\text{E.P.}_m = \frac{2RT}{\mathbf{F}} \ln \frac{a_{\pm_c}}{a_{\pm_m}} = \frac{2RT}{\mathbf{F}} \ln \Delta. \quad . \quad (27)$$

This equation is valid even for a weak electrolyte, since the standard states are fixed by extrapolation of $E_1 + \frac{2RT}{\mathbf{F}} \ln c$

or $E_1 + \frac{2RT}{F} \ln m$ to infinite dilution where dissociation is complete.

The electromotive force, E_2, of the corresponding cell with a metallic electrode in equilibrium with a solution of the metallic salt, MA :

$$\underset{}{M} \quad \underset{a_c \text{ or } a_m}{MA} \quad A,$$

is given by the equation

$$E_2 = {}^{A}\pi_{0_c} - {}^{M}\pi_{0_c} - \frac{2RT}{F} \ln a_{\pm_c}$$

$$= {}^{A}\pi_{0_m} - {}^{M}\pi_{0_m} - \frac{2RT}{F} \ln a_{\pm_m} ;$$

$$\therefore \quad {}^{A}\pi_{0_c} - {}^{A}\pi_{0_m} = {}^{M}\pi_{0_c} - {}^{M}\pi_{0_m} + \frac{2RT}{F} \ln \triangle.$$

But from (25)

$${}^{A}\pi_{0_c} - {}^{A}\pi_{0_m} = {}^{H_2}\pi_{0_c} - {}^{H_2}\pi_{0_m} + \frac{2RT}{F} \ln \triangle ;$$

$$\therefore \quad {}^{M}\pi_{0_c} - {}^{H_2}\pi_{0_c} = {}^{M}\pi_{0_m} - {}^{H_2}\pi_{0_m},$$

or $$ {}^{M}\text{E.P.}_c = {}^{M}\text{E.P.}_m. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Thus the result of employing different activity scales is to change the potentials of the electrodes in the standard states. Since the potential of the standard hydrogen electrode is taken as zero, the differences for both ions are included in the standard potentials of the anions, those of the cations remaining unchanged.

To compare the partial molal free energy contents of a solute in two different solvents some fugacity system must be employed. Let the fugacity of the solute in solvent I be α and its fugacities in the standard states be $\alpha_{0_c} \ldots \alpha_{0_m} \ldots, \alpha_{0_x} \ldots$, then the activities in that solution are given by

$$a_c = \frac{\alpha}{\alpha_{0_c}}, \quad a_m = \frac{\alpha}{\alpha_{0_m}}, \quad a_x = \frac{\alpha}{\alpha_{0_x}}.$$

Similarly, for a given solution of the same solute in the second solvent if the fugacity be β,

$$b_c = \frac{\beta}{\beta_{0_c}}, \quad b_m = \frac{\beta}{\beta_{0_m}}, \quad b_x = \frac{\beta}{\beta_{0_x}},$$

where the activities of the solute are $b_c \ldots, b_m \ldots, b_x \ldots$ in that solution and the fugacities $\beta_{0c} \ldots, \beta_{0_m} \ldots, \beta_{0_x} \ldots$ in the standard state. Then the free energy change on transferring one gram-molecule of solute from the first solution to the second is, by definition, equal to $\mathrm{RT} \ln \frac{\alpha}{\beta}$. Under the special condition that $a_c = b_c$, and therefore $\frac{\alpha}{\beta} = \frac{\alpha_{0_c}}{\beta_{0_c}}$, the free energy of transfer will be the same as when the transfer is made between solutions in the standard states in both solvents. If, on the other hand, the concentration is the same in the two solvents while the activities are now denoted by ${}_c a$ and ${}_c b$, then

$$\operatorname*{Lt}_{c \to 0} \frac{{}_c a}{{}_c b} = \frac{c}{c} = 1.$$

This, as infinite dilution is approached, reduces to the special condition previously mentioned, and hence

$$\frac{\alpha}{\beta} = \frac{\alpha_{0_c}}{\beta_{0_c}}, \quad \ldots \ldots \quad (30)$$

that is, the free energy of transfer between solutions of equal concentration becomes in the limit the same as that between solutions at the respective standard states. This result holds whatever concentration scale is chosen.

When one Faraday is passed through the cell

$$\begin{array}{ccccc} \mathrm{A} & \underset{\substack{\text{in solvent I} \\ a}}{\mathrm{HA}} & \mathrm{H_2}-\mathrm{H_2} & \underset{\substack{\text{in solvent II} \\ b}}{\mathrm{HA}} & \mathrm{A} \end{array}$$

one gram-molecule of solute is transferred from solvent I to solvent II. The e.m.f. of the cell, E_3, is given by the equation

$$\mathrm{E}_3 = {}^{\mathrm{A}}\mathrm{E.P._{II}} - {}^{\mathrm{A}}\mathrm{E.P._{I}} - \frac{2\mathrm{RT}}{\mathbf{F}} \ln \frac{b}{a}. \quad \ldots \quad (31)$$

Thus ${}^{\mathrm{A}}\mathrm{E.P._{II}} - {}^{\mathrm{A}}\mathrm{E.P._{I}}$ is a measure of the change in partial molal free energy of the solute HA when transferred at unit activity from solvent I to solvent II. But from equation (30) it follows that this is also the limiting value as infinite dilution is approached of the change in partial molal free energy of the solute when it is transferred from a solution of concentration c in solvent I to the same concentration in solvent II.

Though this result is equally true whatever the concentration scale, the numerical values are not independent of

the choice of standard states (27), because the allocation of all the standard states involves an extrapolation to infinite dilution, where the partial molal free energy becomes an infinite negative quantity. Moreover, the free energy of transfer from a solution of concentration c to one of $\frac{c}{2}$ becomes, as c tends to zero,

$$\mathrm{RT} \ln \frac{c}{\frac{c}{2}},$$

and thus is equal to RT ln 2, independently of the value of c. All properties at infinite dilution must be expressed in terms of an appropriate ratio which can be made to retain a finite value in the limit where the concentration approaches zero, so that the interpretation of results dependent on extrapolation to infinite dilution must be made with proper regard for the method by which the limit is approached.

Thus the limiting values of the free energy change are given by the following expressions :—

$$\text{From } c \text{ in solvent I to } c \text{ in solvent II} = \mathrm{RT} \ln \frac{\beta_{0_c}}{\alpha_{0_c}},$$

$$\text{,, } m \quad \text{,, } \quad \text{,, } m \quad \text{,, } \quad \text{,,} = \mathrm{RT} \ln \frac{\beta_{0_m}}{\alpha_{0_m}},$$

$$\text{,, } x \quad \text{,, } \quad \text{,, } x \quad \text{,, } \quad \text{,,} = \mathrm{RT} \ln \frac{\beta_{0_x}}{\alpha_{0_x}}. \quad (32)$$

Born * has deduced the free energy in calories of solvation of an ion as the difference in work done in conferring on it a charge $z\epsilon$, first *in vacuo* and then in a solvent of dielectric constant D :

$$\mathrm{F}_i = \frac{z_i^2 \epsilon^2}{2r \cdot \mathrm{J}} \left[1 - \frac{1}{\mathrm{D}}\right], \quad . \quad . \quad . \quad . \quad (33)$$

where J is the mechanical equivalent of heat.

Hence the free energy of transfer of a gram-molecule of a binary electrolyte, the radius of whose ions are r_1 and r_2, from a solvent of dielectric constant D_1 to another in which it is D_2, is given by the equation

$$\Delta \mathrm{F} = \frac{\mathrm{N} \cdot z^2 \epsilon^2}{2 \cdot \mathrm{J}} \left[\frac{1}{\mathrm{D}_2} - \frac{1}{\mathrm{D}_1}\right] \left[\frac{1}{r_1} + \frac{1}{r_2}\right], \quad . \quad . \quad (34)$$

where N is Avogadro's number.

In comparing this equation with the observed electrode potentials it is important to decide which concentration

* Born, *Z. Physik.* xlv. p. 1 (1920).

scale may be appropriately used, as equation (32) shows that their values will depend on the standard state chosen. The derivation of the Born equation merely implies an ion in a large bulk of solvent. The expression is in fact the electrical contribution to the work function, A, of solvation of the ions in very dilute solution, and is independent of the concentration. It thus provides a correction for the deviation from ideal behaviour analogous to the Debye-Hückel activity coefficient, which, in the terms of the previous paper, was shown to be a property of the solution independent of the concentration scale.

The arguments there adduced in favour of the adoption of the volume concentration scale, c', are therefore equally cogent in this case. To these may be added an additional reason. Dalton's law is a statement that the partial molal free energy of one of a mixture of perfect gases depends, at a given temperature, only on its own partial pressure, *i. e.*, its volume concentration. The volume concentration therefore represents a true fugacity scale, being the one on which the free energy of transfer from one mixture to another of the same concentration can, under ideal conditions, be equated to zero. In any solution where a liquid is the solvent, even when the solute is a rare gas, some correction for deviation from ideal behaviour will be necessary. In the case of an electrolyte the Born equation provides another such correction ; clearly then it must be applied to measurements based on such a scale that reference to the ideal state might ultimately be possible.

Summary.

The choice of units of expressing the concentration of solutions has been shown to affect the values of the standard electrode potentials of the anions. From a knowledge of their magnitudes in different solvents the partial molal free energies of transfer of electrolytes in infinitely dilute solution may be calculated and compared with results derived from the Born equation. It is therefore important that a standard unit of concentration be adopted, and, in this connexion, the use of the volume normality scale is advocated.

We wish to express our thanks to Sir Harold Hartley, to whom we are indebted for his advice and criticism in the preparation of these papers.

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XXIII. *An Application of Piezo-electricity to Microscopy.* *By* E. H. Synge*.

A METHOD was suggested by the writer (Phil. Mag. Jan. 1931) by which a microphotograph might be built up on the principle of a telephotograph. It was proposed to obtain the investigating spot of light by using a colloidal particle situated at one focus of an ellipsoid of glass as an illuminating source. Light scattered by the particle and reflected by the surface of the ellipsoid would come to an image, small compared with a wave-length, at the other focus, which was supposed to lie within the microscopic section, and the section was to be moved in two senses, at right angles to one another, relatively to this spot. Reference may be made to the diagram in the article mentioned.

The method was proposed as a photographic one only, but its usefulness would, of course, be greatly increased if it could be converted into a visual one. Practically speaking, the method might be termed a visual one if a picture of the field could be formed on a phosphorescent screen or on very sensitive photographic printing paper, in the course of a few seconds. As the writer proposed it, the motion, in two senses, of the section was dependent on the turning of screws driven by clockwork, and mechanical considerations seemed to set a limit to the rapidity with which a picture might be built up. If we take as the standard size of a picture a square each of whose sides is one hundred times the resolution aimed at, the whole picture would perhaps take half an hour or more to construct. One of the two motions would, of course, be slow and regular, but the other, a to-and-fro motion, would be a hundred times as rapid, and there would be obvious mechanical difficulties to giving this motion by means of screws with any considerable speed, having regard to the regularity and evenness which would be necessary.

No method suggested itself to the writer at that time as an alternative to a mechanical method, but he believes now that the principle of piezo-electricity might be used, and that it would supply all the *desiderata* in the case. Taking formula (7) on page 29 of P. Vigoureux, 'Quartz Resonators and Oscillators' (1931), we have $dt = -\mathrm{H}\frac{t}{e}\mathrm{V}$, where dt is

* Communicated by the Author.

the dilation along the third axis of a quartz crystal, t and e are the thicknesses of the crystal along that axis and the electric axis respectively, H is a constant having the value $6{\cdot}32 \times 10^{-8}$, and V is the difference of potential between plates in contact with the crystal along faces perpendicular to the electric axis. Setting $t=5$ cm. and $e={\cdot}15$ cm., it appears that the change in t for each volt of difference of potential will be about 2×10^{-6} cm. Thus, if the difference of potential increase regularly and constantly through 250 volts, the length of t will change regularly through about 5×10^{-4} cm, which one may take as the dimensions of the field aimed at, in a typical case.

It would therefore only be necessary to incorporate two quartz crystals in the frame (HG in diagram) which carried the section M, in such a way that changes of potential in plates in contact with them would produce changes in the lengths of the crystals, which would have the effect of giving M the motions desired. Or one crystal only might be used to give the more rapid to-and-fro motion, a mechanical method—a screw actuating a wedge—being perhaps more convenient for the slower motion.

The rapidity aimed at is, of course, not very great, and it is easy to suggest mechanical devices by means of a varying resistance by which the potential could be made to vary regularly in whatever way was desired. An electrometer designed for an automatic compensation or null method would no doubt be best for the automatic recording, and it should be noted that the light by which the picture is built up, and which might most conveniently be a strong beam of ultra-violet light, need not be proportional in intensity to the light from F_2, but small differences could be accentuated as desired, which would give the method, either as a visual or a photographic one, a very real advantage over ordinary microscopic methods, in the case of delicate stains, quite apart from the increased resolution attainable. One or two difficulties which might seem to be involved in the writer's suggestion are really not essential ones. Various contact methods are certainly available to test the dimensions of an ellipsoid to well beyond 10^{-6} cm. ; while, to avoid a problem in glass manufacture, the colloidal particle at F_1 might be brought into position on a second glass rod, carried into a hollow in the ellipsoid, the particle simply resting on the surface of the rod, and all interstices being filled with immersion fluid of the right refractive index. It seems worth raising the question also whether a fluorescent particle might not be more advantageous to use than a metal

particle. The light scattered by the former is probably not subject to Rayleigh's law as the size of the particle decreases.

Where rapid results were aimed at, as by the method suggested in the present paper, it might be best that the rod R should be carried right through the ellipsoid and the rapid to-and-fro motion given in the direction of the rod. No doubt various other modifications and improvements would suggest themselves to technicians engaged in constructing the apparatus. But these are matters of detail, and everything required seems to be essentially within the range of present-day technique. The attainable rapidity in the recording apparatus is one of those questions which need hardly be raised at the outset, although it would become of great importance at a later stage. It would presumably depend on the amount of light available, and hence on the resolution.

Note on Fluorescent Particles.—Since writing the above, the writer has found an account by Zsigmondy ('Colloids and the Ultra-Microscope,' p. 196) of the examination of fluorescent substances in extreme dilution which seems remarkable. Zsigmondy, apparently using a not very strong illuminating system (*op. cit.* p. 122), and with heavy losses of light in polarization, found that a light-cone, only 1μ to 2μ thick, was visible, in the case of fluorescein and some other substances, down to a dilution which corresponds to little more than one fluorescent molecule per μ^3 of the aqueous solution. He was, however, unable to see the molecules separately in any case.

In the circumstances it is difficult to think of any reason for his failure except that the molecules were in too rapid and irregular motion for the eye to retain more than an averaged effect. It would certainly seem worth repeating the experiment, using a viscous solution, *e.g.*, of glycerine, in which the molecules would move very slowly, instead of an aqueous one, employing a stronger illuminating system, and perhaps replacing polarization, as a means of separating fluorescent from other scattered light, by a prismatic separation of the different parts of the spectrum, the illuminating beam, of course, in this case, consisting of short wave-lengths only.

Various interesting consequences would follow if the molecules should prove to be visible separately in a sufficiently viscous solution. As regards the microscopic method proposed, it seems a fair conclusion, even from Zsigmondy's

results, that one might look forward to an ultimate development in which a single fluorescent molecule might be the illuminating source, and a resolution of 10^{-7} cm. be attained. It may be remarked that where a fluorescent particle was used it would not be necessary to limit the angle, and hence the intensity of the illuminating beam (supposed of short wave-lengths), since the two parts of the spectrum could be separated afterwards by a prism, even if the original beam were reflected back through the microscopic section M. But, as can easily be seen, the latter contingency might be avoided by the choice of an immersion fluid which, while homogeneous with the glass for the longer wave-lengths, was different for the shorter wave-lengths, a minute prism of this fluid being interposed somewhere in the path of the beam after it had left F_1.

It may also be worth remarking that, if a fluorescent particle were used, the whole method might be inverted—corresponding to dark-field microscopy—the illuminating beam then converging to F_2 and the particle at F_1 being under observation.

XXIV. *An Attempt to Detect High Photoelectric Absorption in Cæsium Vapour at Double the Series Limit.* *By* E. T. S. Appleyard, *Ph.D., H. H. Wills Physical Laboratory, University of Bristol* *.

Introduction.

Bergen Davis † ‡ has, in two recent papers, reported a very high probability of electron capture when α-particles are projected through a cloud of free electrons having certain discrete velocities relative to the α-particle. Briefly, if the kinetic energy of the electron referred to axes fixed in the α-particle is the same as the kinetic energy corresponding to the movement of an electron in a Bohr orbit about the doubly charged helium nucleus, then the electron will be captured into this orbit with a very high degree of probability. In fact, the quantitative work of Barnes suggests that the effective target area for capture under these circumstances can be of the order of 10^{-7} cm.^{2}, which is hundreds of millions of times any known gas kinetic target area.

* Communicated by the Author.

† Bergen Davis and A. H. Barnes, Phys. Rev. xxxiv. p. 152 (1929).

‡ A. H. Barnes, Phys. Rev. xxxv. p. 216 (1930).

This unusually large effective target area is astonishing; for Mohler's * experiments on recombination spectra have shown that capture of electrons, even those whose energy is as small as 1/20 equivalent volt, is relatively improbable when the positive ions of the alkalis are in question. In fact, for electrons of this energy captured into the vacant ground orbit of a cæsium ion the effective target area is about 10^{-20} cm.^{2}.

Moreover (assuming for the moment a stationary helium nucleus), when the electron is captured by a process such as Bergen Davis suggested, there is an energy change in the system which is equal to twice the ionization energy of the orbit into which the electron is captured. This energy must pass out as radiation of double the frequency corresponding to the series limit of ionized helium. There is an exact thermodynamical inverse to this process, viz., the absorption of this frequency by an ionized helium atom and the ejection of a free electron whose kinetic energy is equal to the ionization energy of singly ionized helium. In other words, if we could examine the absorption spectrum of ionized helium, we ought to find, in addition to the ordinary continuous absorption at the series limit, a very powerful absorption band at double this frequency †.

To perform this inverse experiment with ionized helium is, of course, impracticable, but there is no reason to suppose that this process is restricted to ionized helium; for Barnes (*loc. cit.*) reports double capture when the kinetic energy of two electrons is equal to that energy of the ground state of neutral helium. This paper describes an attempt to detect absorption by cæsium vapour in the far ultra-violet in the neighbourhood of twice its series limit.

Experimental.

The series limit of cæsium lies at λ3184. We must therefore look for absorption between λ1500 and λ1600—that is to say, in the region of the spectrum where air begins to to absorb strongly.

This circumstance brought with it some technical problems which were not easy to resolve. The method finally adopted was to place a few drops of cæsium metal in an evacuated

* Mohler and Boëkner, *B. a. Stand. J. Res.* iii. p. 303 (1929).

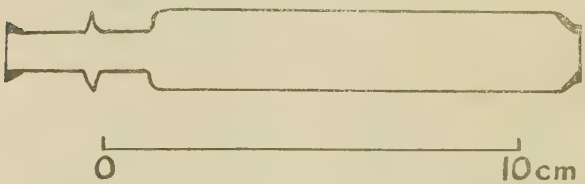
† The band must be fairly broad, for if an exact relative velocity had been necessary for capture, Davis and Barnes (*loc. cit.*) could never have detected it, owing to the distribution-in-velocity of his thermionic electrons and the straggling of his α-particles.

cell with thin quartz windows, and to place this cell (which was provided with a heating element) in the optical axis of a vacuum spectrograph between the slit and a suitable light source.

The absorption cell is shown in fig. 1. The body of the cell was made from pyrex, but its ends were closed by thin quartz windows stuck on with hard enamel. Thin quartz transmits quite satisfactorily down to λ1430 provided it is freshly polished.

The cell was evacuated by means of a diffusion pump and a mercury trap. To remove the water vapour and volatile organic matter from the enamel it was baked out for some time at 200° C. Cæsium was prepared by heating a small quantity of cæsium chromate and misch-metal filings in a metal capsule by electron bombardment. The metallic cæsium produced by the reaction was distilled from the reaction vessel into the cell at about 200° C., and the cell was then

Fig. 1.



sealed off from the reaction vessel and from the pumps. During the distillation the windows were kept free from cæsium metal by local heating, so that finally the cæsium formed a dense mirror in the middle portion of the cell.

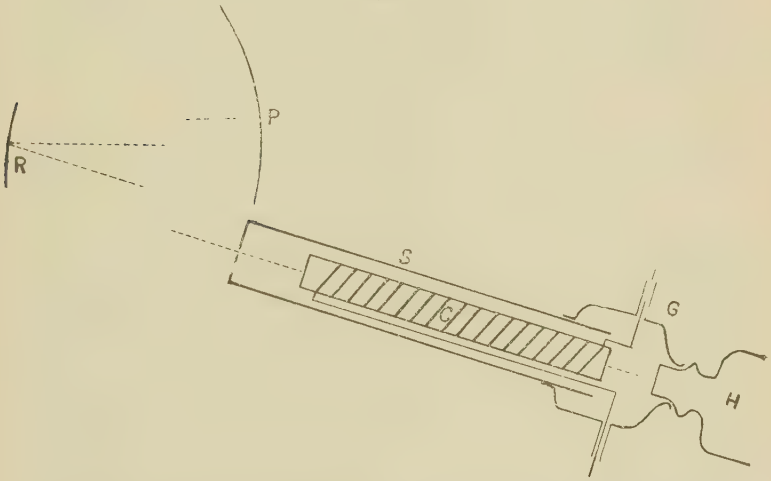
The optical arrangements are shown schematically in fig. 2. To produce the spectra the large vacuum grating spectrograph of the laboratory * was employed in the first order spectrum. The source of light was a water-cooled hydrogen discharge tube, H, dissipating about 1 kilowatt. Pure hydrogen was circulated over charcoal in liquid air and through the tube during the exposures, so as to prevent impurities from showing up in the spectrum.

The absorption cell fitted snugly into a copper tube, C, wound with "nichrome" strip, which was insulated from the body of the tube by mica. Thermocouples at the centre of the tube and at the ends gave the temperature maintained by the heating current, and the windings were arranged to give a temperature difference of about 20° C. between the

* To be described by H. W. B. Skinner elsewhere.

windows and the centre of the cell, so as to keep the former clear from a dew of cæsium metal, which caused much trouble in the earlier experiments. The cell, with its oven, fitted into a water-cooled jacket (not shown), and this into the slit-tube, S, of the spectrograph. The oven was insulated thermally and electrically from the slit-tube by means of glass washers (not shown). Leads for the oven windings and for the thermocouples were taken out to air through the glass adapter, G, which was attached by means of a water-cooled wax joint to the slit-tube. All joints were made vacuum-tight by wax.

Fig. 2.



Spectra were photographed in the first order of the grating R on the curved photographic plate P. The dispersion was about 8·7 A per mm. in the region under consideration, and was ample for the purpose in hand. Oiled plates were used *, and during the exposures the pressure in the spectrograph was kept down to a few thousandths of a millimetre of mercury by means of a fast rotary oil-pump.

Much difficulty was experienced in obtaining suitable conditions for the exposures. The cæsium vapour gradually attacked the quartz windows, producing a surface film which, though transparent to the visible spectrum, absorbed strongly beyond λ 1800.

* Jeantet and Duclos (*cf.* Lyman, 'Spectroscopy of the Extreme Ultraviolet,' p. 61).

The method finally employed was to take an exposure through the cold cell, one through the cell warmed to 100° C., and another again through the cold cell. In this way serious darkening of the windows could be detected. An exposure was also taken with the cell removed from the path of the beam. The lines on the resulting spectra were identified by means of a carbon comparison spectrum and Lyman's * tables.

The best exposed and most uniform plate shows no detectable difference between the second and third spectra mentioned above, and all the spectra examined line for line show a similar intensity distribution. In particular the line λ 1591·5 of molecular hydrogen showed no preferential absorption. Calculation shows that under these experimental conditions an atomic absorption coefficient greater than 10^{-15} would have been readily detected.

Discussion.

If preferential capture of an electron into the ground state of a cæsium ion occurs when the kinetic energy of the electron approaching is equal to the mean kinetic energy of an electron in this orbit, then, just as for capture into a hydrogen-like orbit, radiation of twice the frequency of the series limit must be emitted ; for the calculation demands only that the potential energy of such an orbit shall be double its kinetic energy, and this is always true for a system of electrons and protons †.

An exact argument allows us to calculate the magnitude of the absorption coefficient which we should expect in this neighbourhood.

Let $\psi(\nu_1)$, $\psi(\nu_2)$ be the atomic absorption coefficients in the continuous absorption region of some atom at frequencies ν_1 and ν_2. Then an argument from the "Principle of Detailed Balance" ‡ shows

$$\frac{\psi(\nu_1)}{\psi(\nu_2)} = \frac{{\nu_2}^3}{{\nu_1}^3} \cdot \frac{\nu_1 - \nu_0}{\nu_2 - \nu_0} \cdot \frac{\mathrm{F}(\eta_1)}{\mathrm{F}(\eta_2)},$$

where $\mathrm{F}(\eta_1)$ and $\mathrm{F}(\eta_2)$ are the "target areas" for the exact inverse of the absorption process, viz., for the capture of an electron of energy $\eta = \eta(\nu - \nu_0)$, where ν_0 is the frequency of the series limit.

* Lyman, *loc. cit.*

† Sommerfeld, *Atombau u-Spektrallinien: Anhang.* The above assumption neglects the small perturbation of the core during the core-entering part of the orbit.

‡ Fowler, 'Statistical Mechanics,' p. 478 (Cambridge, 1930).

Let us take for the values of $F(\eta_1)$, $F(\eta_2)$ the values derived from Bergen Davis's experiment and from Mohler's results on the recombination of slow electrons with ions.

Consider absorption of λ 3130 of mercury by cæsium vapour. This will eject from the 1^2S state of cæsium an electron of energy ·06 volts. The target area for recombination of such an electron is at most 10^{-21} cm.^{2}.

This gives (taking the very conservative estimate of 10^{-10} cm.^{2} for the target area in a process such as Bergen Davis describes)

$$\frac{\psi(\nu_1)}{\psi(\nu_2)} \sim 10^{12},$$

if we take ν_1 as the frequency at double the series limit and ν_2 as the frequency corresponding to λ 3130 of mercury. In other words, the absorption at the double series limit should be colossally greater than any previously known continuous absorption. To give numerical values, if we take Mohler's * value for the atomic absorption coefficient of cæsium at λ3130, viz., $K = 1{\cdot}85 \times 10^{-19}$, we obtain for the atomic absorption coefficient at double the series limit

$$K \sim 2 \times 10^{-7}.$$

As we have previously mentioned in the experimental part of the paper a coefficient of absorption $>10^{-15}$ would have been readily detectable.

We conclude that if capture of this type exists in cæsium vapour it must be less than one ten-millionth the magnitude of the effect claimed for α-particles. Davis's results are therefore difficult to understand. They have not been reproduced by Webster †, and a recent note from Bergen Davis ‡ and Barnes appears to throw grave doubt on the validity of his original experimental results ; and since this work was begun Korff and Nickerson § have published a short note in which they report that a similar experiment to the foregoing, using sodium vapour, gave a negative result.

Thanks are due to the various members of this laboratory for help at different times, and to Professor Tyndall for his continued interest. I must particularly thank Dr. H. Jones for helpful discussion. Thanks are also due to the Department of Scientific and Industrial Research for an award, without which this work could not have been performed.

* Mohler and Boëkner, *loc. cit.*
† Webster, Proc. Camb. Phil. Soc. xxvii. p. 116 (1931).
‡ Bergen Davis and Barnes, Phys. Rev. xxxvii. p. 1367 (1931).
§ Korff and Nickerson, Phys. Rev. xxxv. (1930).

XXV. *On the Raman Effect from the Standpoint of Unimolecular Reactions.* *By* A. Ganguli, *Benares Hindu University, Benares* *.

SINCE the discovery of the Raman effect, various theories to explain the mechanism and intensity relationship of Raman lines have been proposed by several authors. Of course, the most satisfactory explanation will be in the line of the dispersion theories developed by Smekal (*Naturw.* xi. p. 873 (1923)), and by Kramers and Heisenberg (*Zeit. f. Phys.* xxxi. p. 684 (1925)). A more powerful method is the wave mechanical (as well as the quantum mechanical) one. A. Carelli (*Atti Acad. Lincei*, ix. p. 165 (1929)) deduces a relationship between the intensities of the anti-Stokes and the Stokes lines from wave mechanics as well as by Dirac's quantum mechanics (see also E. Amaldi, *Atti Acad. Lincei*, ix. p. 876 (1929)). Born (*Naturw.* xvi. p. 673 (1928)), however, suggests that the observed intensities can very well be explained by the statistical application of quantum mechanics. E. G. Kemble and E. C. Hill (Proc. Nat. Acad. Sci. 15, xv. p. 387 (1929)) derive a general formula for the perturbed electric moment associated with the Raman lines using matrix mechanics.

Now a review of the literature indicates two different views of the ratios of the Stokes and the anti-Stokes lines in the Raman effect. Raman (Ind. J. Phys. ii. p. 387 (1928)) believes that the intensities will be proportional to the number of normal and the excited molecules as calculated from the Maxwell-Boltzmann distribution law. Carelli (*loc. cit.*), on the other hand, suggested that the same are proportional to the square of the number of molecules in the normal and the excited states. Again, the fourth power law of intensities was suggested by Cabbanes and Rocard (*J. de Phys. et le Radium*, x. p. 52 (1929)), and later by Mandelstam and Landsberg (*Zeit. f. Phys.* lx. p. 366 (1930)), Tamm (*Zeit. f. Phys.* lx. p. 363 (1930)), and Orstein and Rekveld (*Zeit. f. Phys.* lxiii. p. 257 (1931)). According to these

$$\frac{I_S}{I_{AS}} = \frac{(\nu-\nu)^4}{(\nu+\nu_i)^4}\, e^{\frac{h\nu i}{kT}}, \quad \ldots\ldots \quad (1)$$

where ν is the incident frequency, and ν_i is the difference between the incident and the modified frequencies. Orstein,

* Communicated by K. C. Kar, D.Sc.

as well as Mandelstam and Landsberg, introduces the transition probabilities of Einstein (*Phys. Z.* xviii. p. 123 (1917)), whereas Tamm uses a quantum mechanical expression and deduce the intensities from electric moments.

In the present investigation the Raman effect will be considered from an entirely different aspect. In a previous paper (Phil. Mag. xii. p. 583 (1931)) a mechanism of unimolecular reactions was suggested, and, subsequently, it was pointed out that the Raman effect may be considered as unimolecular reaction, according to the following scheme:

$$A_m \xrightarrow{h\nu} A_{a_1} \longrightarrow A_n + h(\nu - \nu_i) \quad \text{Stokes lines,} \quad . \quad . \quad (2)$$

$$A_n \xrightarrow{h\nu} A_{a_2} \longrightarrow A_m + h(\nu + \nu_i) \quad \text{Anti-Stokes line,} \quad (3)$$

where A_m and A_n stand for a molecule in the mth and nth states. In the first case the normal molecule passes to an intermediate active state by the absorption of radiation of initial frequency ν, and, subsequently, to the excited state by giving out radiation of frequency $\nu - \nu_i$. Thus the excited molecule has absorbed infra-red radiation of frequency ν_i in passing from the state $m \longrightarrow n$. This is in line with the radiation hypothesis of chemical reactions. The difference between the Raman effect and the ordinary chemical reaction is, that, in the first case, the excited (or active) molecules do not further decompose, as in the case of ordinary active molecules, in chemical reactions (*cf.* Phil. Mag. *loc. cit.*). In the case of the anti-Stokes lines we have the reverse process. The molecule already excited absorbs again a quantum of initial frequency ν and thus passes into a second activated state, but immediately returns to the normal state by the emission of radiation of frequency $\nu + \nu_i$.

In order to calculate the number of molecules N_n in the excited state, we will follow a method due to Christiansen (*Zeit. f. Phys. Chem.* ciii. p. 91 (1923)), who advanced arguments similar to that of Einstein (*Phys. Z.*, loc. cit.) in the derivation of Planck's radiation law from the Bohr model. The number of molecules N_{a_1} obtained by the absorption of $h\nu$ by the normal molecules

$$N_{a_1} = N_m \frac{p_{a_1}}{p_m} e^{-\frac{E_{a_1} - E_m}{kT}} = N_m \cdot \frac{p_{a_1}}{p_m} \cdot e^{-\frac{h\nu}{kT}}, \quad . \quad . \quad (4)$$

where the *à priori* probabilities for the two states are p_{a_1} and p_m and $\frac{p_{a_1}}{p_m}$ may be taken to be unity. Now, the number of molecules N_n are obtained by the emission of radiation

of frequency $\nu' = \nu - \nu_1$. Hence, we have, after Einstein, the number of excited molecules,

$$N_n = N_m e^{-\frac{h\nu}{kT}} (A^n_{a_1} + B^n_{a_1} \cdot \rho_{\nu'}), \quad . \quad . \quad . \quad (5)$$

where $A^n_{a_1}$ is the probability of spontaneous emission, and $B^n_{a_1}$ is the probability of emission proportional to the radiation density $\rho_{\nu'}$. Now, we know that (Einstein, *loc. cit.*)

$$\rho_{\nu'} \cdot B^n_{a_1} = \frac{A^n_{a_1}}{e^{\frac{h\nu'}{kT}} - 1}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and hence from (5) and (6),

$$N_n = N_m e^{-\frac{h\nu}{kT}} \cdot \frac{A^n_{a_1}}{1 - e^{\frac{h\nu'}{kT}}}. \quad . \quad . \quad . \quad . \quad (7)$$

If, along with Christiansen, we identify $A^n_{a_1}$ with the frequency ν', then

$$N_n = N_m e^{-\frac{h\nu}{kT}} \cdot \frac{\nu'}{1 - e^{\frac{h\nu'}{kT}}}. \quad . \quad . \quad . \quad . \quad (8)$$

For small values of $\frac{h\nu'}{kT}$, from equation (8), we have

$$N_n = N_m \cdot e^{-\frac{h\nu}{kT}} \cdot \frac{kT}{h}, \quad . \quad . \quad . \quad . \quad (9a)$$

while for larger values of $\frac{h\nu'}{kT}$,

$$N_n = N_m \cdot e^{-\frac{h\nu}{kT}} \cdot \nu'. \quad . \quad . \quad . \quad . \quad . \quad (9b)$$

Hence the total energy due to the Stokes lines

$$E_S = N_n \cdot \rho_{\nu_1}$$
$$= N_m \cdot \frac{k^2T^2}{c^3h} \cdot 8\pi\nu'^2 \cdot e^{-\frac{h\nu}{kT}} \quad . \quad . \quad . \quad . \quad (10a)$$

for high temperatures or small $\frac{h\nu'}{kT}$ (Rayleigh-Jeans). Again,

$$E_S = N_m \cdot \frac{8\pi h\nu_1^4}{c^3} \cdot e^{-\frac{h\nu}{kT}} e^{-\frac{h\nu'}{kT}} \quad . \quad . \quad . \quad (10b)$$

for large values of $\frac{h\nu'}{kT}$ for low temperatures (Wien).

For the case of anti-Stokes transitions we have, similarly, for the number of normal molecules which are brought back to the normal state from the excited state,

$$N_m' = N_n' \cdot {}^{-}e^{\frac{h\nu}{kT}} \cdot \frac{kT}{h},$$

or

$$N_m' = N_n' \cdot e^{-\frac{h\nu}{kT}} \cdot \nu'',$$

where N_n' are the number of previously excited molecules which give rise to N_m' normal molecules by the emission of frequency ν''. Again, since N_n' are obtained by the absorption of energy corresponding to $h\nu_i$, by the normal molecules N_m, we have from Boltzmann's distribution law,

$$N_n' = N_m e^{-\frac{h\nu_i}{kT}} \cdot = N_m e^{-h(\nu-\nu')}\ ;\ \text{since } \nu' = \nu - \nu_i.$$

Thus

$$N_m' = N_m \cdot e^{-\frac{h(\nu-\nu')}{kT}} \cdot e^{-\frac{h\nu}{kT}} \cdot \frac{kT}{h} \cdot \quad . \quad . \quad (11a)$$

or

$$N_m' = N_m \cdot e^{-\frac{h(\nu-\nu')}{kT}} \cdot e^{-\frac{h\nu}{kT}} \cdot \nu'' \cdot \quad . \quad . \quad (11b)$$

$$\therefore \quad E_{AS} = N_m \cdot e^{-\frac{h(\nu-\nu')}{kT}} \cdot c^{-\frac{h\nu}{kT}} \cdot \frac{8\pi\nu''^2k^2T^2}{c^3h} \quad . \quad (12a)$$

for high temperatures or small $\frac{h\nu''}{kT}$, and

$$\therefore \quad E_{AS} = N_m \cdot e^{-\frac{h(\nu-\nu')}{kT}} \cdot e^{-\frac{h\nu}{kT}} \cdot \frac{8\pi k\nu''^4}{c^3} e^{-\frac{h\nu''}{kT}} \quad . \quad (12b)$$

for low temperatures or large $\frac{h\nu''}{kT}$.

Hence, from (10*a*) and (12*a*),

$$\therefore \quad \frac{I_S}{I_{AS}} = \frac{E_S}{E_{AS}} = \frac{\nu'^2}{\nu''^2} \cdot e^{\frac{h(\nu-\nu')}{kT}} = \frac{(\nu-\nu_i)^2}{(\nu+\nu_i)^2} e^{\frac{h\nu_i}{kT}} \cdot \quad (13a)$$

for high temperatures or small ν and ν_i, and from (10*b*) and (12*b*),

$$\frac{I_S}{I_{AS}} = \frac{\nu'^4}{\nu''^4} \cdot e^{\frac{\{h(\nu-\nu_1)+(\nu''-\nu')\}}{kT}} = \frac{(\nu-\nu_i)^4}{(\nu+\nu_i)^4} e^{\frac{3h\nu_i}{kT}} \quad . \quad (13b)$$

for low temperatures or large ν and ν_i, since $\nu' = \nu - \nu_i$ and $\nu'' = \nu + \nu_i$.

If, on the other hand, we take the intensities to be proportional to the number of molecules in the excited and in the normal state as suggested by Raman (*loc. cit.*), we obtain from equations (9 *a*) and (11 *a*),

$$\frac{I_S}{I_{AS}} = e^{-\frac{h\nu_i}{kT}}, \quad . \quad . \quad . \quad . \quad . \quad (14a)$$

and from equations (9 *b*) and (11 *b*),

$$\frac{I_S}{I_{AS}} = \frac{(\nu-\nu_i)}{(\nu+\nu_i)} e^{-\frac{h\nu_i}{kT}} . \quad . \quad . \quad . \quad . \quad (14b)$$

Again, taking the intensities to be proportional to the square of the number of normal and excited molecules (Carelli, *loc. cit.*), we have from the above equations

$$\frac{I_S}{I_{AS}} = e^{-\frac{2h\nu_i}{kT}} . \quad . \quad . \quad . \quad . \quad . \quad (15a)$$

for high temperature or low frequency, and

$$\frac{I_S}{I_{AS}} = \frac{(\nu-\nu_i)^2}{(\nu+\nu_i)^2} . e^{-\frac{2h\nu_i}{kT}} \quad . \quad . \quad . \quad . \quad (15b)$$

for low temperature or large frequency. It is interesting to note that the above equation resembles (13 *a*), although these are valid for different cases. We shall, however, prefer the fourth power formula (13 *b*) for Raman lines in the visible region at ordinary temperature, since ν is sufficiently large. This is in agreement with the results of Mandelstam and others. It may, however, be pointed out that we have $3h\nu_i$ instead of simply $h\nu_i$, in our equation (13 *b*), but this does not make any material difference if $h\nu_i$ is large compared to kT.

My thanks are due to Dr. K. C. Kar for helpful criticism.

Chemical Laboratory,
Benares Hindu University,
Benares, June 1931.

XXVI. *The more Accurate Calculation of the Deflexion of Beams and Struts.* *By* H. H. Jeffcott, *Sc.D.* *

1. In engineering design it is often required to determine by calculation the deflexion of a beam or of a strut, and in some instances this is required with accuracy.

* Communicated by the Author.

We shall suppose the beam or strut to be straight and of uniform section, and to be long compared with the cross-sectional dimensions. Then the solution is to be derived from the formula

$$\frac{EI}{\rho} = M,$$

where M is the value of the bending moment at a point in the axis of the beam where the radius of curvature of the neutral axis is ρ and EI is the flexural rigidity of the beam, E being Young's modulus of elasticity and I the moment of inertia of the cross-section about a line through the neutral axis perpendicular to the plane of bending.

If x and y be the rectangular coordinates of a point on the neutral axis where the radius of curvature is ρ, then

$$\rho = \frac{\left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{3/2}}{\frac{d^2y}{dx^2}}.$$

Hence

$$EI\frac{d^2y}{dx^2} = M\left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{3/2}.$$

Now in general the elastic deformation is small and the slope $\frac{dy}{dx}$ is also small. Accordingly in ordinary calculations it is permissible to neglect the term $\left(\frac{dy}{dx}\right)^2$ compared with unity in the expression

$$\left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{3/2}.$$

The equation

$$EI\frac{d^2y}{dx^2} = M$$

is then usually easily soluble.

When high accuracy is desired this omission is not justifiable, and we shall see, particularly for struts, that the calculated deflexion may be seriously different when such omission is made.

It is proposed in this paper to discuss the deflexion of a simple strut and also of a simple case of bending under lateral load.

In these examples an approximate method will be put forward and illustrated for solving the more exact equation, and it will be found that the results of this method are fully

justified by comparison with the accurate solutions of the exact equations obtained in terms of elliptic integrals.

2. The method of approximation to be employed here has been used by the writer in other * applications.

It consists in first finding the solution of the simple equation

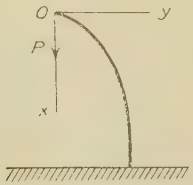
$$\mathrm{EI}\frac{d^2y}{dx^2} = \mathrm{M}.$$

The value of y thus obtained is substituted in the small term $\left(\frac{dy}{dx}\right)^2$ yielding $\left(\frac{dy}{dx}\right)^{\prime 2}$, and a solution is sought of

$$\mathrm{EI}\frac{d^2y}{dx^2} = \mathrm{M}\left\{1+\left(\frac{dy}{dx}\right)^{\prime 2}\right\}^{3/2}.$$

The value of y thus obtained is a closer approximation to the true value than that derived by the complete omission of the small term. If desired this new and more accurate

Fig. 1.



value of y may be substituted in the small term $\left(\frac{dy}{dx}\right)^2$, and a still more accurate value will result.

Successive approximations of this kind may be carried out, but usually only one or at most two will suffice.

The application of the method will be clear from the examples to be given, and its accuracy will be tested by comparison with their exact solutions.

3. Let us take as the first example the case of a long, thin, straight rod clamped vertically at its lower end and subjected to a vertical load P at its upper end.

It is required to study the deflexion, the weight of the rod being negligible (fig. 1).

Take axes of x and y vertically and horizontally through the upper end of the rod as origin, and let x_1 and y_1 be the coordinates of the lower or fixed end.

* See Sci. Proc. R. D. S. xviii. no. 6, pp. 63-66 (1924); and Phil. Mag. vol. viii. p. 66 (July 1929).

Let s be the length measured along the neutral axis of the rod from the origin to the point x, y, and let the whole length of the rod be l. Bending in a single loop will only be considered.

The bending moment at the point xy is Py. The form of the neutral axis is given by

$$EI\frac{d^2y}{dx^2} = -Py\left\{1+\left(\frac{dy}{dx}\right)^2\right\}^{3/2},$$

or, using dots to denote differentiation,

$$EI\ddot{y} + Py(1+\dot{y}^2)^{3/2} = 0.$$

Put $$\mu^2 = \frac{P}{EI};$$

therefore $$\ddot{y} + \mu^2 y(1+\dot{y}^2)^{3/2} = 0.$$

The solution of this equation gives the x, y equation to the neutral axis.

We proceed now to solve this equation in three ways.

4. Firstly, we seek the simple and inexact solution obtained by omitting $\dot{y}^2$. The equation is

$$\ddot{y} + \mu^2 y = 0.$$

This is satisfied by

$$y = y_1 \sin \mu x.$$

The end conditions are

$$\text{at } x=0,\ y=0, \quad \text{at } x=x_1,\ y=y_1 \quad \text{and} \quad \dot{y}=0.$$

Hence we require

$$\mu x_1 = \frac{\pi}{2}.$$

4 (a). We next find an expression for the length of arc s in this simple case.

$$\frac{ds}{dx} = (1+\dot{y}^2)^{1/2} = (1+\mu^2 {y_1}^2 \cos^2 \mu x)^{1/2}.$$

Now the term $\dot{y}^2$ is always small; hence we observe that $\mu^2 {y_1}^2$ is small.

Put $\mu y_1 = 2k$, and expand the radical in powers of k.

Therefore

$$\frac{ds}{dx} = 1 + 2k^2 \cos^2 \mu x - 2k^4 \cos^4 \mu x + \ldots$$

Regard the fourth and higher powers of k as being negligibly small.

Therefore

$$s = (1+k^2)x + \frac{k^2}{2\mu}\sin 2\mu x,$$

the constant of integration being zero, since $s=0$ at $x=0$.

Now $s=l$ when $x=x_1$, and $\mu x_1 = \frac{\pi}{2}$.

Therefore $$l = (1+k^2)x_1 + \frac{k^2}{2\mu}\sin 2\mu x_1 ;$$

$$\therefore \quad \mu l = (1+k^2)\frac{\pi}{2}.$$

For comparison with other solutions it is convenient to put $y = y_1 \cos\theta$, so that here $\sin\mu x = \cos\theta$ and $\mu x = \frac{\pi}{2} - \theta$ Accordingly

$$\mu s = (1+k^2)\left(\frac{\pi}{2} - \theta\right) + \frac{1}{2}k^2 \sin 2\theta.$$

5. For the second method of solution we use successive approximations.

In the equation

$$\ddot{y} + \mu^2 y(1+\dot{y}^2)^{3/2} = 0$$

we substitute in the small term $\dot{y}^2$ the value $y = y_1 \sin\mu x$ obtained in paragraph 4, and solve the resulting equation for y, namely

$$\ddot{y} + \mu^2 y(1+\mu^2 y_1{}^2 \cos^2\mu x)^{3/2} = 0.$$

Now this equation is not readily soluble, and it is more convenient to transform the original equation to one having y as the independent variable, *i. e.*, to an equation in

$$\frac{dx}{dy} \quad \text{and} \quad \frac{d^2x}{dy^2}.$$

The equation $$\ddot{y} + \mu^2 y(1+\dot{y}^2)^{3/2} = 0$$

then becomes $$\ddot{x} + \mu^2 y \dot{x}^3 \left(1 + \frac{1}{\dot{x}^2}\right)^{3/2} = 0.$$

We observe that $\ddot{x} = \mu^2 y \dot{x}^3$ is satisfied by $\mu x = \sin^{-1}\frac{y}{y_1}$.

As an approximation we substitute this value of x in the small term $\frac{1}{\dot{x}^2}$, and we obtain

$$\frac{\ddot{x}}{\dot{x}^3} = \mu^2 y\{1 + \mu^2(y_1{}^2 - y^2)\}^{3/2}.$$

Now we know that the term $\mu^2(y_1^2-y^2)$ is always small compared with 1.

Expanding the radical we have

$$\frac{\ddot{x}}{\dot{x}^3} = \mu^2 y\left\{1+\frac{3}{2}\mu^2(y_1^2-y^2)+\ldots\right\}.$$

Hence

$$-\frac{1}{2}\frac{d}{dy}\left(\frac{1}{\dot{x}^2}\right) = \mu^2 y\left\{1+\frac{3}{2}\mu^2(y_1^2-y^2)\right\}$$

if powers of $\mu^2(y_1^2-y^2)$ higher than the first be omitted.

Integrating we obtain

$$-\frac{1}{\mu^2\dot{x}^2} = y^2\left(1+\frac{3}{2}\mu^2 y_1^2\right)-\frac{3}{4}\mu^2 y^4+\mathrm{C}.$$

When $y=y_1$, $\dot{x}=\infty$;

$$\therefore \quad \mathrm{C} = -y_1^2-\frac{3}{4}\mu^2 y_1^4;$$

$$\therefore \quad \frac{1}{\mu^2\dot{x}^2} = (y_1^2-y^2)+\frac{3}{4}\mu^2(y_1^2-y^2)^2.$$

Put $y=y_1\cos\theta$, and $\mu y_1 = 2k$;

then
$$\frac{1}{\dot{x}^2} = 4k^2\sin^2\theta+12k^4\sin^4\theta\ ;$$

$$\therefore \quad \frac{1}{\dot{x}} = 2k\sin\theta.(1+3k^2\sin^2\theta)^{1/2},$$

or

$$\mu dx = \frac{-2k\sin\theta\, d\theta}{2k\sin\theta.(1+3k^2\sin^2\theta)^{1/2}},$$

since

$$dy = -y_1\sin\theta\, d\theta\ ;$$

$$\therefore \quad \mu dx = -\{1+3k^2\sin^2\theta\}^{-1/2}\ .\ d\theta.$$

Expanding the radical in powers of k, and omitting k^4 and higher powers, since k is small, we obtain

$$-\mu dx = \left(1-\frac{3}{2}k^2\sin^2\theta\right)d\theta\ ;$$

$$\therefore \quad -\mu x = \left(1-\frac{3}{4}k^2\right)\theta+\frac{3}{8}k^2\sin 2\theta+\mathrm{C}.$$

At $\quad x=x_1, \quad y=y_1, \quad \cos\theta=1, \quad \theta=0\ ;$

$$\therefore \quad \mathrm{C} = -\mu x_1\ ;$$

$$\therefore \quad \mu(x_1-x) = \left(1-\frac{3}{4}k^2\right)\theta+\frac{3}{8}k^2\sin 2\theta.$$

When $\qquad x=0, \quad y=0 \quad \text{and} \quad \theta=\frac{\pi}{2}$;

therefore

$$\mu x_1=\left(1-\frac{3}{4}k^2\right)\frac{\pi}{2}.$$

5 (*a*). Next we find an expression for the length of arc s. We have

$$\left(\frac{ds}{d\theta}\right)^2=\left(\frac{dx}{d\theta}\right)^2+\left(\frac{dy}{d\theta}\right)^2;$$

$$\therefore \quad \mu^2\left(\frac{ds}{d\theta}\right)^2=\left\{1-\frac{3}{4}k^2+\frac{3}{4}k^2\cos 2\theta\right\}^2+4k^2\sin^2\theta$$

$$=1+k^2\sin^2\theta;$$

$$\therefore \quad -\mu\frac{ds}{d\theta}=1+\frac{1}{2}k^2\sin^2\theta \text{ approximately};$$

$$\therefore \quad -\mu s=\left(1+\frac{1}{4}k^2\right)\theta-\frac{1}{8}k^2\sin 2\theta+C.$$

When $\qquad y=0, \quad \text{or} \quad \theta=\frac{\pi}{2}, \quad s=0$;

therefore

$$C=-\left(1+\frac{1}{4}k^2\right)\frac{\pi}{2};$$

$$\therefore \quad \mu s=\left(1+\frac{1}{4}k^2\right)\left(\frac{\pi}{2}-\theta\right)+\frac{1}{8}k^2\sin 2\theta.$$

$$s=l \quad \text{when} \quad \theta=0;$$

$$\therefore \quad \mu l=\left(1+\frac{1}{4}k^2\right)\frac{\pi}{2}.$$

This result differs seriously from that obtained by the simple though rough method of paragraph 4 (*a*). In that case

$$k^2=\frac{2\mu l}{\pi}-1$$

or

$$y_1^2=\frac{4}{\mu^2}\left(\frac{2\mu l}{\pi}-1\right).$$

The more approximate method followed in this paragraph eads to

$$y_1^2=\frac{16}{\mu^2}\left(\frac{2\mu l}{\pi}-1\right),$$

In other words, the value of the maximum deflexion is double that obtained by the simple method.

It is therefore important to investigate the matter with still greater accuracy.

Incidentally this great difference in the deflexion as determined from the two equations suggests the carrying out of an experiment of this kind to determine if $\frac{EI}{\rho} = M$ is in fact the more accurate formula. It is to be noted, however, that in this position the deflexion is very sensitive to small changes in the value of the load, which must therefore (as well as E and I) be determined with accuracy.

6. We now turn to finding a more exact solution of the equation

$$\ddot{y} + \mu^2 y(1+\dot{y}^2)^{3/2} = 0.$$

Obviously we can write down a first integral.

Multiply across by $\frac{2\dot{y}}{(1+\dot{y}^2)^{3/2}}$, and we obtain on integration

$$\frac{1}{(1+\dot{y}^2)^{1/2}} = \frac{1}{2}\mu^2 y^2 + C.$$

Now $\dot{y} = 0$ at $y = y_1$; therefore $C = 1 - \frac{1}{2}\mu^2 y_1^2$.

Hence

$$\frac{1}{(1+\dot{y}^2)^{1/2}} = 1 - \frac{1}{2}\mu^2(y_1^2 - y^2).$$

Put $y = y_1 \cos\theta$, $\mu y_1 = 2k$, and reduce.

Therefore

$$-\mu dx = -\frac{1-2k^2\sin^2\theta}{\sqrt{1-k^2\sin^2\theta}}\,d\theta$$

$$= 2\sqrt{1-k^2\sin^2\theta}\,.\,d\theta - \frac{d\theta}{\sqrt{1-k^2\sin^2\theta}};$$

$$\therefore \quad \mu x = F(k, \theta) - 2E(k, \theta),$$

where F and E are elliptic integrals of the first and second kinds.

Since k is small compared with unity, we may expand the radicals, and if we omit powers of k higher than the second we find

$$-\mu x = \int\left(1 - \frac{3}{2}k^2\sin^2\theta\right)d\theta$$

$$= \left(1 - \frac{3}{4}k^2\right)\theta + \frac{3}{8}k^2\sin 2\theta + C.$$

When $x = x_1, \quad y = y_1, \quad \cos\theta = 1, \quad \theta = 0;$

therefore $C = -\mu x_1;$

$$\therefore \quad \mu(x_1 - x) = \left(1 - \frac{3}{4}k^2\right)\theta + \frac{3}{8}k^2 \sin 2\theta.$$

When $x = 0, \quad y = 0 \quad \text{and} \quad \theta = \frac{\pi}{2};$

$$\therefore \quad \mu x_1 = \left(1 - \frac{3}{4}k^2\right)\frac{\pi}{2}.$$

6 (*a*). To find an expression for the length of arc s we proceed precisely as in paragraph 5 (*a*).

Since the values of x and y in terms of θ are exactly the same in paragraphs 5 and 6 to the second power of k, we obtain the same results for s and l as in paragraph 5 (*a*), namely

$$\mu s = \left(1 + \frac{1}{4}k^2\right)\left(\frac{\pi}{2} - \theta\right) + \frac{1}{8}k^2 \sin 2\theta,$$

and $$\mu l = \left(1 + \frac{1}{4}k^2\right)\frac{\pi}{2}*.$$

Accordingly to the second power of k the value of the maximum deflexion y_1 obtained from the equation

$$\ddot{y} + \mu^2 y(1 + \dot{y}^2)^{3/2} = 0$$

agrees with that obtained by the method of approximation described, using but one stage in the approximation, and is double that obtained by solving the simpler equation

$$\ddot{y} + \mu^2 y = 0.$$

In like manner the solution may be carried to higher powers of k than the second, and the exact solution be compared with that obtained by the method of approximations, employing one or more successive stages as desired.

7. We now turn to a second example and consider a simple case of lateral loading.

We shall find the deflexion of a long, thin, straight beam clamped horizontally at one end and subjected to a single load W at the other end, the weight of the beam being negligible (fig. 2).

Take axes of x and y horizontally and vertically through the loaded end of the beam, $x_1 y_1$ being the coordinates of the clamped end.

Let s be the length of the arc of the neutral axis from

* This result has recently been given by M. Bertrand de Fontviolant.

the origin to the point x_1y_1, and let the whole length of the beam be l.

The bending moment at the point xy is Wx, and accordingly the form of the neutral axis is given by

$$EI\frac{d^2y}{dx^2} = -Wx\left\{1+\left(\frac{dy}{dx}\right)^2\right\}^{3/2},$$

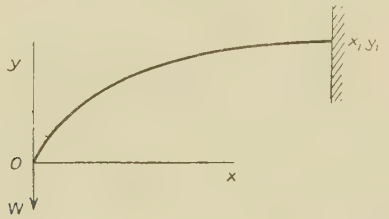
or
$$\ddot{y} + 2\mu x(1+\dot{y}^2)^{3/2} = 0,$$

if
$$\mu = \frac{W}{2EI}.$$

We proceed to solve this equation in three ways in paragraphs 8, 9 and 10.

8. First we take the simple and usual method of omitting the term $\dot{y}^2$. The equation is then $\ddot{y}+2\mu x = 0$.

Fig. 2.



We readily find the solution complying with the terminal conditions is

$$y = \frac{1}{3}\mu x(3x_1^2 - x^2).$$

Hence
$$y_1 = \frac{2}{3}\mu x_1^3.$$

8 (*a*). To find s

$$ds = (1+\dot{y}^2)^{1/2}.dx,$$

$$\dot{y} = \mu(x_1^2 - x^2).$$

Hence

$$ds = \left\{1 + \frac{1}{2}\dot{y}^2 - \frac{1}{8}\dot{y}^4 + \ldots\right\} dx$$

$$= \left\{1 + \frac{1}{2}\mu^2(x_1^2 - x^2)^2 - \frac{1}{8}\mu^4(x_1^2 - x^2)^4 + \ldots\right\} dx\ ;$$

$$\therefore \quad s = x + \frac{1}{2}\mu^2 x\left(x_1^4 - \frac{2}{3}x_1^2x^2 + \frac{1}{5}x^4\right)$$

$$- \frac{1}{8}\mu^4 x\left(x_1^8 - \frac{4}{3}x_1^6x^2 + \frac{6}{5}x_1^4x^4 - \frac{4}{7}x_1^2x^6 + \frac{1}{9}x^8\right) + \ldots ;$$

$$\therefore \quad l = x_1 + \frac{4}{15}\mu^2 x_1^5 - \frac{16}{315}\mu^4 x_1^9 + \ldots .$$

9. We next apply the method of approximations to this problem.

In the equation

$$\ddot{y} + 2\mu x(1+\dot{y}^2)^{3/2} = 0$$

we substitute in the small term $\dot{y}^2$ the approximate value of y already obtained in paragraph 8.

Hence

$$\ddot{y} + 2\mu x\{1 + \mu^2(x_1^2 - x^2)^2\}^{3/2} = 0.$$

As $\dot{y}^2$ and therefore $\mu^2(x_1^2 - x^2)^2$ is always small, we may expand and omit the higher powers of the small quantity.

Hence

$$\ddot{y} + 2\mu x\left\{1 + \frac{3}{2}\mu^2(x_1^2 - x^2)^2\right\} = 0.$$

Integrating and substituting the terminal conditions we readily find

$$y = \frac{1}{3}\mu x(3x_1^2 - x^2)$$

$$+ \frac{1}{70}\mu^3 x(35x_1^6 - 35x_1^4x^2 + 21x_1^2x^4 - 5x^6),$$

and

$$y_1 = \frac{2}{3}x_1^3 + \frac{8}{35}\mu^3 x_1^7.$$

9 (*a*).

$$ds = (1+\dot{y}^2)^{1/2}dx$$

$$= \left(1 + \frac{1}{2}\dot{y}^2 - \frac{1}{8}\dot{y}^4 + \ldots\right)dx$$

$$= \left\{1 + \frac{1}{2}\mu^2(x_1^2 - x^2)^2 + \frac{3}{8}\mu^4(x_1^2 - x^2)^4 + \ldots\right\}dx,$$

since y has the value found in paragraph 9.

$$\therefore \quad s = x + \frac{1}{2}\mu^2 x\left(x_1^4 - \frac{2}{3}x_1^2x^2 + \frac{1}{5}x^4\right)$$

$$+\frac{3}{8}\mu^4 x\left(x_1^8-\frac{4}{3}x_1^6x^2+\frac{6}{5}x_1^4x^4-\frac{4}{7}x_1^2x^6+\frac{1}{9}x^8\right)+\ldots,$$

and

$$l=x_1+\frac{4}{15}\mu^2x_1^5+\frac{16}{105}\mu^4x_1^9+\ldots.$$

10. Finally, in verification of the method of approximation just employed we seek a more exact solution of the original equation

A first integral of the equation

$$\ddot{y}+2\mu x(1+\dot{y}^2)^{3/2}=0$$

is

$$\frac{\dot{y}}{(1+\dot{y}^2)^{1/2}}+\mu x^2=\mathrm{C}.$$

At $x=x_1$, $y=0$; therefore $\mathrm{C}=\mu x_1^2$.

Therefore

$$\frac{\dot{y}}{(1+\dot{y}^2)^{1/2}}=\mu(x_1^2-x^2).$$

Hence

$$\dot{y}=\frac{\mu(x_1^2-x^2)}{\{1-\mu^2(x_1^2-x^2)^2\}^{1/2}}.$$

The solution of this equation can be expressed in elliptic integrals.

Since the term $\mu^2(x_1^2-x^2)^2$ is small it will suffice to obtain an approximate solution of the first integral by expansion and the omission of small quantities. It then becomes approximately

$$\dot{y}=\mu(x_1^2-x^2)\left\{1+\frac{1}{2}\mu^2(x_1^2-x^2)^2\right\}.$$

Hence

$$y=\frac{1}{3}\mu x(3x_1^2-x^2)+\frac{1}{70}\mu^3x(35x_1^6-35x_1^4x^2+21x_1^2x^4-5x^6),$$

and

$$y_1=\frac{2}{3}\mu x_1^3+\frac{8}{35}\mu^3x_1^7.$$

10 (*a*).

$$ds=(1+\dot{y}^2)^{1/2}dx,$$

$$1+\dot{y}^2=\frac{1}{1-\mu^2(x_1^2-x^2)}$$ from paragraph 10;

$$\therefore\quad ds=\left\{1+\frac{1}{2}\mu^2(x_1^2-x^2)^2+\frac{3}{8}\mu^4(x_1^2-x^2)^4+\ldots\right\}dx;$$

$$\therefore \quad s = x + \frac{1}{2}\mu^2 x\left(x_1^4 - \frac{2}{3}x_1^2x^2 + \frac{1}{5}x^4\right)$$
$$+ \frac{3}{8}\mu^4 x\left(x_1^8 - \frac{4}{3}x_1^6x^2 + \frac{6}{5}x_1^4x^4 - \frac{4}{7}x_1^2x^6 + \frac{1}{9}x^8\right)$$
$$+ \ldots,$$

and

$$l = x_1 + \frac{4}{15}\mu^2 x_1^5 + \frac{16}{105}\mu^4 x_1^9 + \ldots .$$

11. Thus we find that the results of the method of approximation of paragraph 9, even when employing only one stage of approximation, are the same as those given by the more exact method of paragraph 10, so far as the terms up to μ^4 are concerned.

The usual simple method of paragraph 8 gives agreement only so far as terms in μ^2.

For obtaining exact results in deflexion problems the usual method involving the omission of the term $\dot{y}^2$ is insufficient, and the employment of the method of successive approximation described above, even when carried only to one stage, is advocated as a method of general utility.

June 1931.

XXVII. *Notices respecting New Books.*

L'Introduction des théories de Newton en France au XVIII^e siècle. By Pierre Brunet. (Paris: Librairie Albert Blanchard. Price 55 francs.)

IN this book the learned author describes the protracted struggle between the followers of Des Cartes and Newton which preceded the general acceptance of the latter's philosophy, to use the old term, in France. The action-at-a-distance of Newton offered grave difficulties to philosophers accustomed to think of space as filled with vortices which carried the planets round; as Voltaire wrote in 1733: "Un Français qui arrive à Londres trouve les choses bien changées en philosophie .... Il a laissé le monde plein, il le trouve vide. A Paris, on voit l'univers composé de tourbillons de matière subtile: à Londres, on ne voit rien de cela. Chez nous, c'est la pression de la lune qui cause le flux de la mer; chez les Anglais, c'est la mer qui gravite vers la lune." The Cartesians reproached Newton with bringing back, in the force of gravity, the doctrine of occult qualities, although as Cotes (whom M. Brunet, with that pleasant variation which the French always bring to our names, calls Côtes) and Newton himself

pointed out, the term would be more properly applied to the vortices of fictive material than to a force which was manifest to everybody, however little its true nature was understood.

Newton's criticism of the vortices, on the ground that they were incompatible with the known laws of astronomy, was met with a host of ingenious, but mechanically unsound, arguments, hypotheses, and analogies, described by M. Brunet in his first chapter. The next chapter deals with the period 1720 to 1728, in which appeared not only Keill's famous exposition of the Newtonian doctrine, written in Latin, Coste's French translation of the 'Opticks,' and 's Gravesande's textbook of Newtonian philosophy, but also a host of books defending various aspects of the Cartesian theory. In 1728 the Académie des Sciences awarded a prize to Bülffinger for a Cartesian disquisition on gravity, and Privat de Molières defended the vortex scheme, while in the next few years other writers showed that the Cartesian philosophy still had a firm hold in France. We then find the great names of Maupertius and Voltaire, who were to bring about the ultimate triumph of Newton in France. Meanwhile, however, Jean Bernoulli defended the Cartesian system, of which he was an upholder until his death in 1748. M. Brunet deals at length with these matters, bringing to their discussion a wealth of knowledge, and closes his book in the year 1738, when Voltaire's 'Eléments de la Philosophie de Newton' appeared, to give the controversies a new direction. He promises to continue the history of the subject in a further volume.

M. Brunet's book is of very great interest, showing, as it does, how great is the force of a tradition, and how possible it is for men of great learning, nay even of genius, to adhere to a theory which has, seen from a distance, clearly been shown to be untenable. Every student of the history of science will find his subject one of great fascination. Many of the arguments of the Cartesians would be easier to follow if M. Brunet had given us a few drawings in illustration of their contentions, which are, no doubt, perfectly clear to him, saturated as he must be in the Cartesian literature of the time. A copious bibliography will aid the reader who wishes to go more deeply into any particular point.

A Comprehensive Treatise upon Inorganic and Theoretical Chemistry. By J. W. Mellor. Vol. IX. (London: Longmans, Green & Co. Price 63*s*.)

Dr. Mellor's monumental undertaking is by now so well known to all physicists and chemists that praise, or expressions of wonder at so colossal a task so well carried out, are superfluous. The present volume deals with the elements tellurium, chromium, molybdenum, and tungsten, all of great interest to physicists. The tradition of excellence and completeness which already attaches to the work appears to be well maintained.

The Nature of a Gas. By Leonard B. Loeb. (New York: John Wiley & Sons. Price 12*s.* 6*d.*)

The plan of this book is somewhat unusual. It owes its origin to a Committee on Electrical Insulation of the American National Research Council, which, in view of the fact that gases are commonly used as insulators, asked Professor Loeb to treat of the nature and electrical properties of a gas. It is probably as a consequence of the fact that the book is not primarily intended for physicists that it contains not only, for example, a general account of some of the latest researches on the probability of ionization of different gases and vapours by the impact of electrons of different primary velocity, but also a simple description of the kinetic theory of gases, including the significance of mean free path and other elementary conceptions which would generally be supposed to be familiar to readers seeking information on ionization. The matter is, from the point of view of the ordinary text-book or monograph, miscellaneous, but the exposition is at all points very good and the diagrams excellent.

The book is divided into three sections. The first one presents a general outline of the modern theory of atomic structure, in terms of electron orbits, and of the elementary features of molecular structure, as seen by the physicist. The second gives a description of the chief features of the kinetic theory of gases, while in the third the mechanism of ionization is discussed, with special reference to critical potentials. Throughout the language is simple and the mathematics elementary. There are useful appendices and a short and practical bibliography. The peculiar object with which the book was written seems to have been well fulfilled.

Molecular Rays. By Ronald G. J. Fraser, Ph.D. (Aberd.). [Pp. xii+204.] (Cambridge University Press, Fetter Lane, London, E.C. 4. Price 12*s.* 6*d.* net.)

The increasingly large number of experimental results that have been obtained by using molecular rays makes Dr. Fraser's book particularly welcome at the present stage. The earlier part of the book deals in considerable detail with the technique of the production and measurement of the rays, and gives valuable information on laboratory experience which has not yet appeared in the original papers on the subject. A considerable amount of the research recorded has been carried out at the Hamburg Institute of Physical Chemistry, in which the author himself worked for three years.

A good account is given of the important bearing of the method of molecular rays on the fundamental postulates of the gas kinetic theory. Attention is drawn to the direct and primitive nature of the method which enables it to attack problems of a fundamental character. This is strikingly demonstrated by the fact that it has been found possible to diffract beams of atoms and molecules

at the cross grating of a crystal cleavage, and thus to establish directly the wave properties demanded by the new mechanics. The last chapter touches many applications of molecular rays, but gives rather a brief account of the processes involved. Mathematical data are treated where possible in an elementary manner, and are everywhere as concise as is possible to bring out the full significance of the results. Diagrams, graphs, and photographs are used freely throughout the book with a very pleasing effect. Full references to researches carried out until 1930 are given as footnotes, and the subject matter is developed up to and including that year. A specialist will find 'Molecular Rays' a useful text-book, while other people, with but a slight knowledge of the subject, will read it with enjoyment and profit.

Numerical Examples in Physics. By W. N. Bond, M.A. (Cantab.), D.Sc. (Lond.). [Pp. 127.] (Edward Arnold & Co., London. Price 4*s*. net.)

Elementary students of physics have no difficulty in finding sets of examples which enable them to test their understanding of the formal results of the subject. An urgent need has, however, been felt for similar typical examples in the more advanced parts, particularly in the modern developments. The present little volume sets out to supply this need. There are 450 examples in all, of which 141 are of the standard to be expected in an Honours Degree, 227 of a somewhat lower standard, and the remainder elementary. The examples have been well selected, and there are but few that should cause difficulty to a student who has studied his text-books intelligently. It is particularly gratifying to find a chapter of numerical questions on atomic physics, and it is to be hoped that in future editions this last chapter will be considerably enlarged. It would also be desirable to add a group of questions on spectral theory and spectro-photometry, so as to familiarize the student with energy and term values and modern spectroscopic notation. A table of constants and useful formulæ would also be an advantage. For teaching purposes this book should be invaluable.

Acoustics: a Text on Theory and Application. By George W. Stewart, Ph.D., and Robert B. Lindsay, Ph.D. [Pp. iv+358, 142 figures.] (Messrs. Chapman & Hall, Ltd., 11 Henrietta St., Covent Garden, London, W.C. 2. Price 25*s*. net.)

This book sets out to give a detailed theoretical survey of the advance of acoustics during the last decade as a result of the many new applications to which acoustical devices have been put, *e. g.*, subaqueous signalling, loud-speakers, and the use of sound in national defence. A clear exposition is given of the theory underlying the modern applications, as may be seen in the chapters dealing with acoustic transmission through conduits, the effects of branch lines, acoustic coupling, and so forth. The analogy with

electrical circuits is emphasized and skilfully used. On the other hand, the chapters on physiological acoustics, acoustics of buildings, and atmospheric acoustics give the impression of having been dealt with rather cursorily.

The idea inspiring the work, however, seems to be rather to deal with problems from their theoretical aspect, and to leave the field clear to others to give detailed descriptions of the practical devices already used or which can be constructed on the lines predicted by theory. Much of the practical information regarding acoustic impedance, filtration of sound, and so forth is the result of research by the authors.

Although in the preface the authors deny a thread of mathematical continuity throughout the book, and maintain that each application stands alone, yet in reading the work the impression is conveyed of a central mathematical idea which is enlarged and explained from Chapter I. to Chapter X. In some cases, where the full theory is already given in Rayleigh's 'Sound,' it has only been considered necessary to give a shortened synopsis and references. From Chapter IX. to the end the theory is obviously introduced only to explain certain special applications, and here gives the impression of discontinuity. Since, however, this is not a treatise on mathematics, but on the most concrete of the modern sciences, the feeling of physical unity must be the ultimate goal.

The claim put forward by the authors in the preface, that "the present work is unique in its stress on the important researches of the past decade and in the useful combination of material both from the theoretical and practical viewpoints," can hardly be substantiated in the light of the appearance of Dr. A. B. Wood's treatise on the subject.

Some useful examples are appended to each chapter. This will be found helpful to students entering the higher examinations, while much of the theory will inspire researchers in radio-telephony and telegraphy and many other subjects which have sprung up during the last decade.

XXVIII. *Proceedings of Learned Societies*

GEOLOGICAL SOCIETY.

November 4th, 1931.—Prof. E. J. Garwood, M.A., Sc.D., F.R.S., President, in the Chair.

1. Mr. E. J. Wayland, A.R.C.S., F.G.S., gave a brief description, illustrated by lantern-slides, of the Katwe crater-lake, Uganda. He remarked that Lake Katwe occupies the bottom of an explosion crater of the caldera type, and is one of many in southern Busongora lying between Lakes Edward and George, on the south and east respectively, and Ruwenzori

on the north-west. Not only is it of interest as a type example, but also because it is the source and centre of a flourishing native-managed salt industry, the improvement of which is being considered by the Government.

The level of Lake Katwe in relation to that of Edward, was wrongly determined by the Boundary Commission of 1906, and, very recently, was quite differently, and again erroneously, given by a railway survey party. The lecturer's own figures differed from the first of these determinations by nearly 170 feet, and from the second by about 102 feet. The difference in each case was enormous and very important, for upon it, in his view, depended the true geological and economic significance of Katwe. Precise re-levelling undertaken by the railway authorities had shown the lecturer's figures to be correct.

Lake Edward, it had been found, oscillates in accordance with the sunspot cycle, while Lake Katwe does not. While the level of the former is above the water-table, that of the latter is determined and maintained by it. It had been further shown that, although the volcanic vent passes through the saturation zone, its upper parts are more or less completely sealed off from the surrounding ground-water by deposits of the less soluble salts thrown out of solution at successively lower levels as temperature decreased with time. Within the tube so formed, aqueous circulation is produced by the temperature gradient, and the most soluble of the salts, derived at depth from decomposing alkali lavas, are thereby brought to the surface and, as a consequence of solar evaporation, are deposited in the shallow lake.

2. ' Petrology of the Volcanic Fields East and South East of Ruwenzori, Uganda.' By Prof. Arthur Holmes, D.Sc., D.I.C., F.G.S., and Henry Francis Harwood, Ph.D., M.Sc., F.G.S.

The various suites of rocks with which this paper deals were collected in 1924 and 1930 by members of the Geological Survey of Uganda, and were sent to the Authors for description and analysis, together with relevant field-notes and a geological map.

Towards the close of the period in which the Kaiso lacustrine beds were deposited, volcanic activity broke out along a series of belts extending north and south of Fort Portal and north and south of the Kazinga Channel. The first phase (Lower to Middle Pleistocene) is represented by sub-aqueous tuffs. Post-Kaiso rifting movements followed, and were succeeded in turn by a second phase of vulcanism, in which explosion-vents were blown through the rift-valley floor, the bordering scarps, and the adjoining plateau. The rocks of this stage

include tuffs and agglomerates, ejected blocks, and volcanic bombs.

Throughout the area the earlier tuffs appear to represent melilite-basalts. They contain fragments of biotite-pyroxenites and related types which constitute a well-defined suite of sub-volcanic rocks. The tuffs are followed by others having compositions transitional towards that of leucitite. The later cognate ejected blocks include melanocratic varieties of potash-nephelinite and leucitite, most of which are referred to as potash-ankaratrite or leucite-ankaratrite. Accompanying them are bombs of leucitite and olivine-leucitite, some of the latter being sufficiently rich in olivine to be regarded as a volcanic equivalent of kimberlite.

The volcanic belts together constitute a co-magmatic region of a highly individualized kind. Positive evidence is provided by the community of field occurrences, rock assemblages, mineral associations, and geochemical characters. Negative evidence includes the absence of quartz, plagioclase, and amphiboles from the suite of minerals, and of basalts and basaltic derivatives from the rocks. An attempt is made to show that the rocks could not have been derived from basaltic magma by any known process of differentiation, with or without assimilation. On the other hand, the rarer constituents revealed by five chemical analyses, and in particular the abundance of BaO and SrO, suggest community of origin with kimberlite, a new and detailed analysis of which has been made by Mr. L. S. Theobald for comparison.

It is shown that both kimberlite and olivine-leucitite could be derived from a magma having the composition of average peridotite or stony meteorites by abstracting from it the constituents of dunite and eclogite in reasonable proportions. Continued abstraction of olivine and pyroxene would lead to leucitite. Enstatite is found to be an early product of crystallization from olivine-leucitite; it also occurs as phenocrysts in melilite-basalt. These facts suggest the possibility that the abstraction of olivine and enstatite from a primary peridotite magma would serve to provide a melilite-basalt magma. The early separation of enstatite leaves the magma markedly deficient in silica, while under conditions of higher pressure the separation of chloromelanite (in eclogite) removes soda and leaves a relatively potash-rich magma. The hypothesis is proposed that the rocks described, together with kimberlite, represent various stages in the high-pressure crystallization-differentiation of a parent magma having a composition akin to that of average peridotite. The substratum that underlies the 'basaltic layer' is regarded as the probable source of this magma.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]